AD-A073 828 BAIRD CORP BEDFORD MA GOVERNMENT SYSTEMS DIV F/G 7/2
A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS,(U)
MAY 79 J T BROWNRIGG, D A BUSCH, L P GIERING DOT-CG-81-78-1888
USCG-D-53-79 NL

UNCLASSIFIED

1 OF 3

AD A073828

REPORT NO. CG-D-53-79

A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS

J. T. Brownrigg
D. A. Busch
L. P. Giering
Baird Corporation
Government Systems Division
125 Middlesex Turnpike
Bedford, MA 01730

CONDUCTED UNDER CONTRACT DOT-CG-91-78-1888

U.S. Coast Guard Research and Development Center
Avery Point, Groton, Connecticut 06340

May 1979

FINAL REPORT

PREPARED FOR

U. S. DEPARTMENT OF TRANSPORTATION
UNITED STATES COAST GUARD

OFFICE OF RESEARCH AND DEVELOPMENT
WASHINGTON D. C. 20590

N O T I C E

This document is disseminated under the sponsorship of the Department of Transportation in the interest of information exchange. The United States Government assumes no liabiility for its contents or use thereof.

The United States Government does not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the object of this report.

The contents of this report reflect the views of the Coast Guard Research and Development Center, which is responsible for the facts and accuracy of data presented. This report does not constitute a standard, specification, or regulation.

D. L. Birkimer

DONALD L. BIRKIMER, Ph.D., P.E.
Technical Director
U.S. Coast Guard Research and Development Center
Avery Point, Groton, Connecticut 06340

(18) USCG, CGR/DC (19) D-53-79, 15/79

Technical Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
CG-D-53-79		

4. Title and Subtitle
(6) A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS.

5. Report Date
(11) May 1979

6. Performing Organization Code

8. Performing Organization Report No.
(12) 273p.

7. Author(s)
(10) J. T. Brownrigg, D. A. Busch, L. P. Giering

9. Performing Organization Name and Address
Baird Corporation
Government Systems Division
125 Middlesex Turnpike
Bedford, MA 01730

10. Work Unit No. (TRAIS)

11. Contract or Grant No.
(15) DOT-CG-81-78-1888

13. Type of Report and Period Covered

12. Sponsoring Agency Name and Address
Department of Transportation
U.S. Coast Guard
Office of Research and Development
Washington, DC 20590

14. Sponsoring Agency Code

15. Supplementary Notes
The contract under which this report was submitted was under the technical supervision of the Coast Guard Research and Development Center, Groton, CT 06340. R&D Center Report Number CG R&DC 15/79.

16. Abstract
Room temperature luminescence (fluorescence) spectra of ninety-six toxic and hazardous materials corrected for instrument response and light output are presented. Eight additional spectra of non-fluorescent toxic and hazardous materials are also included. A brief literature review, estimated detection limits and a spectral code for preliminary identification of these materials are also provided.

17. Key Words	18. Distribution Statement
Toxic and Hazardous Materials Fluorescence Luminescence	Document is available to the U.S. public through the National Technical Information Service, Springfield, VA 22161

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
UNCLASSIFIED	UNCLASSIFIED		

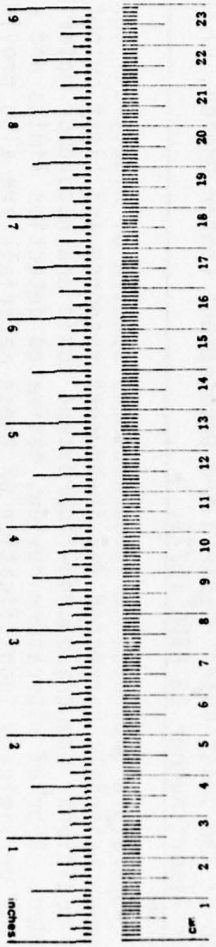
Form DOT F 1700.7 (8-72) Reproduction of form and completed page is authorized

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
	LENGTH			
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
	AREA			
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
	MASS (weight)			
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
	VOLUME			
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
	TEMPERATURE (exact)			
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
	LENGTH			
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
	AREA			
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
	MASS (weight)			
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
	VOLUME			
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
	TEMPERATURE (exact)			
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

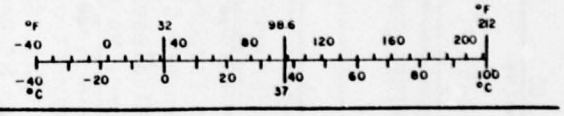


TABLE OF CONTENTS

TABLE OF CONTENTS (con't.)

LIST OF TABLES

LIST OF TABLES (con't.)

LIST OF FIGURES

1. INTRODUCTION

This final report, prepared for the United States Coast Guard Research and Development Center at Groton, Connecticut, summarizes work performed by Baird Corporation on Contract No. DOT-CG-81-78-1888. Room temperature luminescence (fluorescence) spectra of 100 toxic and hazardous materials are presented. In addition, a brief literature review, estimated detection limits and a spectral code for preliminary identification of these materials are given.

The Coast Guard is charged with the responsibility of protecting the nation's waterways from accidental or deliberate discharge of petroleum products and other toxic and hazardous materials. In order to provide the capability to detect, identify and quantify hazardous substances found in navigable waterways, the Coast Guard intends to develop an in-house system of analytical techniques to handle this problem. It is the purpose of this report to demonstrate the utility of luminescence data for the identification and quantitation of hazardous materials and hopefully contribute to a successful methodology for a difficult problem.

The high sensitivity of luminescence plus the specificity afforded by the two spectral signatures of excitation and emission suggest that luminescence may afford a relatively simple and inexpensive approach to the identification of a significant fraction of unknown hazardous materials.

2. PREVIOUS WORK

As part of this contract, a brief literature review to determine existing corrected emission spectra for comparison with those developed in the program was conducted. This literature search was expanded to include both corrected and uncorrected emission and excitation spectra as well as available absorption spectra and fluorescence quantum yields.

In Table 1 previously published absorption spectra are tabulated. It was necessary to collect this data for as many of the 100 toxic and hazardous materials studied in this contract to compare with the absorption spectra obtained in our laboratories for these materials. Absorption spectra, taken on the toxic and hazardous materials, were used to aid in the selection of the appropriate concentration and excitation wavelength for fluorescence measurements and to check the purity by comparison with published data, of the compounds furnished by the Coast Guard. Compounds supplied by the Coast Guard which did not agree with the published data are tabulated in Section 4 of this report.

In Table 2 previously published uncorrected and corrected fluorescence spectra and fluorescence quantum yields are tabulated. This careful review of the literature showed that there exists very little corrected fluorescence data, especially for the hundred or more materials of interest to the Coast Guard. Where possible a comparison was made (same or similar solvent and concentration) with published corrected fluorescence spectra and corrected spectra obtained in this contract. The discussion of this comparison can be found in Section 4.

TABLE 1. PREVIOUSLY PUBLISHED ABSORPTION SPECTRA

	Compound	Solvent	Reference
1.	acenaphthene	cyclohexane	5
		ethanol	9
		methanol	21
2.	acetone	ethanol	4
3.	acridine	ethanol	5,9
		methanol	21
4.	aniline	ethanol	5
		cyclohexane	5,21
		isooctane	9
5.	anisoyl chloride	cyclohexane	21
6.	anthracene	cyclohexane	5,9,21
		methanol	10
		ethanol	11
		isooctane	11
7.	1,2 benzanthracene	ethanol	9,10
		pentane	12
	(benz(a)anthracene)	methanol	21
8.	benzene	cyclohexane	5,9,21
		benzene	5
		vapor	21
9.	benzenesulfonic acid	methanol	21
		methanol/KOH	21
		methanol/HCl	21
10.	benzo(g,h,i)fluoranthene	cyclohexane	5
11.	benzonitrile	cyclohexane	21
12.	benzo(a)pyrene	ethanol	10
		dioxane	21
		methanol	19
13.	benzoyl chloride	cyclohexane	21
14.	benzyl alcohol	cyclohexane	5
		ethanol	5,14
		methanol	21
15.	benzylamine	isooctane	9
		methanol	21

TABLE 1. PREVIOUSLY PUBLISHED ABSORPTION SPECTRA (con't)

	Compound	Solvent	Reference
16.	benzyltriethyl ammonium chloride	methanol	21
17.	brucine	methanol	21
18.	p-tert-butylphenol	cyclohexane	21
19.	catechol	cyclohexane	9
		methanol	21
20.	m-chloroaniline	methanol	21
21.	p-chloroaniline	methanol	21
22.	1-chloronaphthalene	methanol	21
23.	2-chloronaphthalene	cyclohexane	5
24.	p-chlorophenol	methanol	21
25.	p-chlorotoluene	cyclohexane	21
26.	4-chloro-o-toluidine	methanol	21
27.	chrysene	cyclohexane	5
		ethanol	5,9
		methanol	10,21
		pentane	12
28.	m-cresol	cyclohexane	9
		methanol	21
29.	o-cresol	cyclohexane	9
		methanol	21
		methanol/KOH	21
30.	p-cresol	cyclohexane	5,9
		ethanol	5
		methanol	21
31.	cumene	cyclohexane	21
32.	cymene	cyclohexane	21
33.	dibenz(a,h)anthracene	benzene	5
		ethanol	9
		methanol	10
34.	dichlorodiphenylsilane	methanol	21

TABLE 1. PREVIOUSLY PUBLISHED ABSORPTION SPECTRA (con't)

	Compound	Solvent	Reference
35.	2,4-dichlorophenol	methanol	21
		methanol/KOH	21
36.	2,4-dimethylphenol (2,4-xylenol)	cyclohexane	9
		methanol	21
37.	3,5-dimethylphenol	methanol	21
38.	4,6-dinitro-o-cresol	methanol	21
39.	2,4-dinitrophenol	ethanol	24
		methanol	21
40.	diphenylamine	cyclohexane	21
41.	diphenylether	methanol	21
42.	1,1-diphenylhydrazine	methanol	21
43.	2,4-di-tert-butylphenol	methanol	21
		methanol/KOH	21
44.	2,6-di-tert-butylphenol	methanol	21
45.	dowtherm (4-biphenylylphenylether)	methanol	21
46.	2,4-di-sec-butylphenol	cyclohexane	5
		methanol	21
47.	fluoranthene	cyclohexane	5
		methanol	21
48.	gallic acid, hydrate	methanol	21
49.	hydroquinone	methanol	21
50.	n-methylaniline	methanol	21
51.	α-methylstyrene	cyclohexane	21
52.	naphthalene	cyclohexane	5
		ethanol	9
		methanol	21
53.	1-naphthylamine	cyclohexane	5,21
		ethanol	5,9,14

TABLE 1. PREVIOUSLY PUBLISHED ABSORPTION SPECTRA (con't)

	Compound	Solvent	Reference
54.	2-nitroaniline	ethanol	24
		hexane	24
		water	24
		.01 M NaOH	24
		methanol	21
55.	o-nitrophenol	methanol	21
		methanol/KOH	21
56.	phenol	cyclohexane	5,9
		methanol	5
57.	p-nonylphenol	cyclohexane	21
58.	quinoline	ethanol	5
		cyclohexane	9
59.	resorcinol	ethanol	9
		methanol	21
60.	salicylic acid	ethanol	11
61.	styrene	cyclohexane	5,21
62.	tannic acid	methanol	21
63.	1,2,3,4,-tetrahydro-naphthalene	methanol	21
64.	toluene	cyclohexane	5,9
		methanol	21
65.	p-toluenesulfonic acid	methanol	21
66.	o-toluidine	isooctane	9
67.	p-toluidine	cyclohexane	21
68.	1,3,5-triethylbenzene	cyclohexane	5
		methanol	21
69.	m-xylene	cyclohexane	5,21
70.	o-xylene	cyclohexane	5,21
71.	p-xylene	cyclohexane	5,21

TABLE 2. PREVIOUSLY PUBLISHED FLUORESCENCE SPECTRA AND QUANTUM YIELDS

	Compound	Quantum Yield	Solvent	Fluorescence Spectrum	Ref.
1.	acenaphthene	0.6(8)*	cyclohexane	corrected em	(5)
		0.31(7)	hexane		
		0.39(6)	ethanol		
2.	acetone		ethanol	uncorrected em	(4)
		.01±.003(2)	hexane	corrected em	(20)(25)
3.	acridine		ethanol	corrected em	(5)
4.	aniline	0.08(5)(8)	cyclohexane	corrected em	(5)
		0.08(2)	ethanol	corrected em	(5)
			vapor	uncorrected em	(4)
5.	anthracene	0.35(5)	cyclohexane	corrected em	(5)
			methanol	corrected em	(5)(10)
		0.27(7)(26)	ethanol	corrected em	(15)(26)
		0.31(7)	hexane		
6.	1,2 benzanthracene		methanol	uncorrected em	(13)
			diethylether	uncorrected em	(17)
		0.20(6)	ethanol		
		0.20(2)	hexane		
7.	benzene	0.07(5)	cyclohexane	corrected em	(5)
			neat	corrected em	(5)
		0.04(7)	hexane		
		0.04(6)(26)	ethanol	corrected em	(26)
8.	benzo(g,h,i)fluoranthene	0.30(5)	cyclohexane	corrected em	(5)
9.	benzo(a)pyrene		ethanol	corrected ex/em	(10)
			methanol	uncorrected ex/em	(19)
10.	benzyl alcohol	0.08(5)	cyclohexane	corrected em	(5)
			ethanol	corrected em	(5)
11.	t-butylphenol		methanol	uncorrected em/ex	(16)
12.	catechol		water	uncorrected em/ex	(16)
13.	p-chloroaniline	0.017(22)	water		
14.	1-chloronaphthalene		cyclohexane	uncorrected em/ex	(16)
		0.058(2)	ethanol-ether-77°K		
15.	2-chloronaphthalene		cyclohexane	corrected em	(5)
16.	p-chlorophenol	0.0089(22)	water		

TABLE 2. PREVIOUSLY PUBLISHED FLUORESCENCE SPECTRA AND QUANTUM YIELDS (con't)

Compound	Quantum Yield	Solvent	Fluorescence Spectrum	Ref.
17. p-chlorotoluene	0.02(18)	ethanol		
18. chrysene	0.14(5)	cyclohexane	corrected em	(5)
	0.17(6)	ethanol	corrected em	(5)
		methanol	corrected ex/em	(10)
		pentane	corrected em	(12)
19. o-cresol		vapor	uncorrected em	(4)
20. m-cresol	0.25(23)	water		
21. p-cresol	0.09(5,8)	cyclohexane	corrected em	(5)
		ethanol	corrected em	(5)
	0.088(8)	water		
22. dibenz(a,h)anthracene		benzene	corrected em	(5)
		methanol	corrected ex/em	(10)
23. 2,4-dimethylphenol		methanol	uncorrected ex/em	(16)
24. diphenylamine		cyclohexane	uncorrected ex/em	(16)
25. dowtherm (4-biphenylyl-phenyl-ether)	0.09(8)	cyclohexane		
26. ethylbenzene	0.18(8)	cyclohexane	corrected em	(5)
27. fluoranthene	0.30(8)	cyclohexane	corrected em	(5)
		methanol	corrected ex/em	(10)
28. gallic acid,hydrate		water	uncorrected ex/em	(16)
			uncorrected em	(15)
29. hydroquinone		water	uncorrected ex/em	(16)
30. methoxychlor		ethanol	uncorrected em	(15)
31. naphthalene	0.23(5)	cyclohexane	corrected em	(5)
	0.10(1)	hexane	uncorrected ex/em	(16)
	0.205(1)	polar		
	0.19(26)	ethanol	corrected em	(26)
32. 1-naphthylamine	0.38(8)	cyclohexane	corrected em	(5)
		ethanol	corrected em	(5)
33. (PCB) 4,4-dichloro-biphenyl		cyclohexane	uncorrected ex/em	(16)

TABLE 2. PREVIOUSLY PUBLISHED FLUORESCENCE SPECTRA AND QUANTUM YIELDS (con't)

Compound	Quantum Yield	Solvent	Fluorescence Spectrum	Ref.
34. phenol	0.066(8)	cyclohexane	corrected em	(5)
		methanol	corrected em	(5)
	0.22(15)	water		
	0.19(26)	ethanol	corrected em	(26)
35. quinoline		ethanol	corrected ex/em	(5)
36. salicylic acid, sodium salt		.0001N KOH	uncorrected ex/em	(16)
37. styrene		cyclohexane	corrected ex/em	(5)
38. toluene	0.17(5)	cyclohexane	corrected em	(5)
	0.23(7)	hexane		
39. p-toluidine		cyclohexane	uncorrected ex/em	(16)
40. 1,3,5-triethyl-benzene	0.12(5)	cyclohexane	corrected ex/em	(5)
41. uranyl acetate	0.04(15)	water		
42. uranyl sulfate		acid solution		(6)
43. m-xylene	0.17(8)	cyclohexane	corrected ex/em	(5)
44. o-xylene	0.19(8)	cyclohexane	corrected ex/em	(5)
45. p-xylene	0.40(8)	cyclohexane	corrected ex/em	(5)
	0.20(1)	polar		

*The numbers in parentheses are reference numbers for quantum yield measurements.

3. EXPERIMENTAL

3.1 Samples and Sources

Table 3 contains a list of the chemicals used in this contract. Included in this list is the supplier of the chemical and the grade of the chemical used.

TABLE 3. CHEMICAL SOURCE LIST

Compound	Source	Purity
acenaphthene	Fluka	purum
acetone	Chem Service, Inc.	high purity
acridine	Fluka	≥ 98%
aniline	Fluka	99.5%
anisoyl chloride	MCB	--
anthracene	Fluka	≥ 99%
Aroclor 1242 1254	RFR Corporation	--
atrazine	Chemical Service	99%
azinphosmethyl	Chemical Service	96%
benz(a)anthracene	McKay	--
benz(a)pyrene	Aldrich	98%
benzene	Chemical Service	high purity
benzonitrile	Chemical Service	high purity
benzoyl chloride	Fluka	99.5%
benzyl alcohol	Chemical Service	high purity
benzyl amine	Fluka	≥ 99%
benzyl amine	MCB	--
benzyltriethylammonium chloride	MCB	practical
Bisphenol A	Aldrich	--
brucine	Fluka	purum
butylbenzylphthalate	Chemical Service	--
o-tert-butylphenol	Aldrich	99%
p-tert-butylphenol	Fluka	~99%
carbaryl	Chemical Service	--
carnauba wax	Fisher	#1 yellow
castor oil	MCB	USP
catechol	Chemical Service	high purity
4-chloroaniline	Fluka	≥ 99%

TABLE 3. CHEMICAL SOURCE LIST (con't)

Compound	Source	Purity
1-chloronaphthalene	Fluka	≥ 99%
4-chlorophenol	Fluka	≥ 99%
chloropyrifos	Chemical Service	98.5%
4-chlorotoluene	RFR Corporation	--
4-chloro-o-toluidine	MCB	practical
chrysene	Duke	(standard)
coconut oil	---	--
cod liver oil	Squibb	--
copper naphthenate	Chemical Service	lab assist.
cottonseed oil	---	--
coumaphos	Chemical Service	99%
o-cresol	Fluka	≥ 99%
p-cresol	Fluka	≥ 99%
cumene	Chemical Service	high purity
p-cymene	Chemical Service	high purity
DDD	RFR Corporation	--
DDT	RFR Corporation	--
diazinon	Chemical Service	92.4%
1,2,5,6-dibenzanthracene	Baird sample	--
dicamba	Chemical Service	94%
dichlone	Chemical Service	98%
dichlorobenil	Chemical Service	97%
diethylbenzene	Chemical Service	tech.
diethylene glycol	Fluka	≥ 99%
diethylphthalate	MCB	--
2,4-dimethyl phenol	Aldrich	99%
3,5-dimethyl phenol	Chemical Service	high purity
dimethyl terephthalate	Chemical Service	high purity
2,4-dinitroaniline	Fluka	puriss
4,6-dinitrocresol	Fluka	practical
2,4-dinitrophenol	Fluka	puriss, 20% H_2O
diphenylamine	Fluka	≥ 99%

TABLE 3. CHEMICAL SOURCE LIST (con't)

Compound	Source	Purity
diphenyldichlorosilane	Chemical Procurement Lab	
diphenylhydrazine	Fluka	puriss
diquat dibromide	Chemical Service	98%
diuron	Chemical Service	99%
dodecylbenzene	Fluka	≥ 97%
dowtherm	---	--
ethylbenzene	Chemical Service	high purity
fluoranthene	RFR Corporation	--
gallic acid	Fluka	≥ 99%
hydroquinone	Fluka	≥ 99%
indene	Fluka	≥ 90%
lard	Armour Star	--
linseed oil	Grumbacker	artist quality
methylene di-p-phenylene isocyanate	MCB	--
methylisobutylketone	Chemical Service	--
α-methylstyrene	Chemical Service	--
naphthalene	Fluka	puriss
α-naphthylamine	Chemical Procurement Lab	--
nitralin	Chemical Service	98%
m-nitroaniline	Chemical Service	high purity
nonylphenol	Chemical Service	--
olive oil	Filliop berio, Italy	pure
palm oil	---	--
parathion K	Chemical Service	98%
peanut oil	---	--
phenol	Fluka	≥ 98%
phenyl ether	Fluka	≥ 97%
phthalic acid	Fluka	puriss
piperazine anhydride	Fluka	puriss
polyethylated nonylphenol	Chemical Service	lab assist.

TABLE 3. CHEMICAL SOURCE LIST (con't)

Compound	Source	Purity
pyrogallol	Chemical Service	high purity
quinoline	Fluka	≥ 99%
sodium dodecylbenzene sulfonate	Chemical Service	lab assist.
soya bean oil	---	--
styrene	Chemical Service	high purity
tannic acid	Chemical Service	practical
1,2,3,4-tetrahydro naphthalene	Fluka	≥ 97%
p-toluidine	Fluka	≥ 99%
toluene		≥ 99.5%
p-toluene sulfonic acid		99%
1,1,1-trichloro-2,2-bis (p-methoxyphenyl)ethane Methoxychlor	Chemical Service	98.3%
tricresylphosphate	Chemical Service	tech.
1,3,5-triethylbenzene	Fluka	purum
trifluralin	Chemical Service	99%
turpentine	MCB	--
undecylbenzene	Chemical Procurement Labs	--
uranyl nitrate	Chemical Service	lab regent
m-xylene	Eastman Kodak	--
o-xylene	Chemical Service	high purity
zirconium acetate	Chemical Service	--

3.2 Sample Preparation

During preliminary discussion with Coast Guard personnel, cyclohexane was selected as the primary solvent. If a particular compound was not soluble in cyclohexane, the following solvents were to be tried in order: water, methanol, ethanol, and acetonitrile. This was the order observed, with minor exceptions as noted below. The cyclohexane used was Matheson, Coleman, and Bell spectroquality grade. Variation in purity was noted between lots, although within a given lot good consistency was found. In general those lots currently available having the lowest background were used. The following lots of spectroquality cyclohexane were used: 10H24, K1H29B, and 6J23I. The water used was produced by a commercial (Continental Water Company) deionizing system equipped with particulate and carbon filters. The water produced by this system had a very low fluorescence background, comparable to that of distilled water. Samples of water from the deionizing system were run on the Baird spectrofluorimeter prior to running any toxic and hazardous materials. Commercially available ethanol (Graves, 95%) had fewer fluorescent impurities than methanol, and was used exclusively. (The solvation power of these two should be quite similar.)

The hazardous materials were weighed by difference into sample bottles equipped with screw caps and Teflon liners using an analytical balance. The balance was originally kept in the hood, but the front face velocity of the air moving in the hood make exact weighings difficult. The balance was moved to a special exhaust hood and set on a piece of granite. The balance used is accurate to $\pm$5% at the 1 mg level, which was the weight range required for preparation of the stock solution. All sample bottles were allowed to come to equilibrium at the laboratory temperature before any weighings were made. Solvent volumes of 10 ml were added to the sample bottles using disposable pipettes (accuracy $\pm$1%). All hazardous materials were handled with care. Gloves and laboratory coats were worn by personnel in handling

these materials. All samples were prepared in the hood and all waste was disposed of properly.

Sample bottles were made of glass and had plastic screw caps with Teflon liners. Bottles were cleaned by soaking overnight in a dichromate - sulfuric acid bath, then scrubbed with a detergent solution (Micro) and rinsed with hot tap and deionized water. After oven drying, the bottles were rinsed with a portion of cyclohexane and dried with a stream of nitrogen gas. Teflon liners were cleaned with detergent solution, water, and then oven dried.

Solutions were stored in a refrigerator until being used. Generally, solutions more than one week old were discarded and a fresh solution prepared. Whenever possible, the solutions were run within one day of being prepared. Except for photochemical instabilities noted below, stock solutions of toxic and hazardous materials were stable.

3.3 Data Acquisition

Primary data consisted of both fluorescence and absorption spectra. Although absorption spectra were not specified in the original contract, they were considered important for two reasons. First, these provided an estimate of optimum excitation wavelengths, which is especially important for weak emitters. Second, these provide information on the purity of the material and thus, the origin of the observed emission. Many absorption spectra have been cataloged by Sadtler (21), and this data provided additional insights as to the purity of the materials studied.

A primary objective of this study was to obtain fluorescence spectra on one hundred toxic and hazardous materials. More

than one hundred compounds were obtained, of which several showed no detectable fluorescence, but an attempt was made to provide fluorescence spectra for one hundred materials.

3.3.1 Absorption Spectra

All absorption spectra were obtained using a Cary 14 double-beam spectrophotometer. Sample and reference (pure solvent) solutions were contained in standard 1 cm path quartz cuvettes. This spectrophotometer uses a hydrogen lamp in the ultraviolet (200-400 nm) and a tungsten-halogen lamp in the visible (400-700 nm) region. Serial ten-fold dilutions were made until the principal absorption bands were in the 0-2 absorbance range.

3.3.2 Fluorescence Spectra

Fluorescence spectra were obtained on a Baird FC-100 Fluoricord spectrofluorimeter, equipped with an A/D converter and a PDP-8A computer. This system was originally structured for recording spectra in octal format on teletype paper tape, which could then be converted to computer cards. The card input was in turn used by an IBM 1130 computer for generating total luminescence spectra (TLS) in contour format. Spectral correction and graphics were accomplished using an IBM 1130 computer with Calcomp plotter. Additional details of this procedure are published elsewhere (27,28). In principle, this system could have been modified to produce corrected spectra in real time, without use of the IBM 1130 computer. The approach used, however, did have the advantage that the corrected spectra were available in digital format, facilitating data reduction.

The fluorimeter was equipped with a Hamamatsu R446 photomultiplier tube, whose response extended from approximately 185 to 870 nm. The wavelength range available on the Spectrofluorimeter is 200-

750 nm for both excitation and emission. A beam splitter located in the sample compartment, near the excitation slit, deflected a small portion of the excitation light through a quartz diffuser plate and onto a Hamamatsu 1P28 photomultiplier tube. This provided a reference ("monitor") signal proportional to the lamp intensity. A standard 150 watt Hanovia xenon lamp was used for the source.

Spectral bandwidths, selected in consultation with Coast Guard personnel, were 10 nm in excitation and 2 nm in emission. For this survey, it was decided to keep the analyzing (emission) slits reasonably narrow in order to resolve vibronic structure. Before actually running the toxic and hazardous materials for this contract a study of the effect of changing slit width on the spectrum of pyrene and anthracene was performed. In the case of pyrene the structure is very well defined when 10,10, 1,1 slits are used. However, if 10,10,2,2 slits are used there is little loss in fine structure and a gain of at least a factor of four in signal. Changing the slits to 5,5,5,5 results in a gain in signal of over a factor of 10 but there is significant loss of structure. However, many of the compounds have structureless or less fine structure in emission, so that better sensitivities could have been achieved using greater slit widths (this also applied to the excitation bandwidth). Anthracene at .11 ppm in cyclohexane was run under varying slit conditions. The results are tabulated below.

TABLE 4. THE EFFECT OF SLIT WIDTH ON A .11 PPM ANTHRACENE SIGNAL IN CYCLOHEXANE

Slit Setting	Relative Signal at 380 nm
10,10,1,1	99
10,10,2,2	468
10,10,5,5	2700
10,10,10,10	9100
5,5,1,1	33
5,5,2,2	143
5,5,5,5	820

In this case there was no significant loss in structure and in most cases there is significant gains in signal intensity.

The monochromator scan speed was 1 nm/sec., and the sample and monitor signals (two four-digit octal values) were teletyped and punched every second. Thus, data was taken at approximately 1 nm increments throughout the scan. Originally, a maximum wavelength span of 280 nm was possible (the limitations being available computer core memory), but this was later increased to 350 nm. Data collection on a particular scan was stopped when the apparent intensity had fallen to the background level, as established during preliminary scans. At the end of a scan, the source shutter was closed and several additional data points taken to establish appropriate dark current signals. These values were then subtracted from the preceding data prior to applying the correction factors (see below).

For each sample, at least two scans were recorded. If these appeared identical, they would be separately corrected and plotted. To improve signal-to-noise, the sum of these two scans was also plotted. If the two scans appeared to be different, a third scan was obtained, and the two most similar scans were retained. In this report, only the summed scans are reproduced in the Compendium.

The excitation wavelength chosen represented a compromise between reasonable intensity and freedom from scatter excitation light. This generally resulted in the use of a shorter excitation wavelength than the maximum excitation wavelength. In some cases use of the maximum excitation wavelength produced spectra that were distorted by scatter (Rayleigh and Raman) on the short wavelength side. For estimating detection limits, however (Section 3.4.1), the apparent excitation maximum was used.

3.3.2.1 Standards

Three fluorescence standards were selected for periodic measurment during the data collection phase of the contract. These standards were intended to function as reference materials in the calculation of detection limits, and also serve as monitors of instrumental sensitivity and calibration over long periods of time.

The three standards selected were naphthalene, anthracene, and fluoranthene at concentrations of 10, 1, and 1 ppm respectively in cyclohexane. These were originally run at weekly intervals as a check of the constancy of the calibration. No relative spectral changes were noted, so the frequency of measurement was extended to two weeks. Over the five month period during which data was taken, no significant (>2%) changes were observed in the relative intensities of the standards.

To obtain a daily measure of instrument sensitivity, and particularly lamp intensity, the cyclohexane Raman bands were recorded at excitation wavelengths of 250, 275, 300, and 350 nm. This procedure was followed prior to running a particular sample in the same cuvette, and also served as check of solvent purity and cuvette cleanliness. The wavelengths chosen spanned the excitation region most frequently used to excite the sample.

3.3.2.2 Fluorimeter Calibration

Fluorimeter calibrations involved the monochromator wavelengths and responsivity of the emission monochromator. The procedures used are detailed below.

Wavelength calibrations were performed with a low-pressure mercury lamp utilizing reference lines recommended by the ASTM (29). The emission monochromator was calibrated first. The lamp, in an aluminum housing equipped with a pinhole aperture

(to reduce light intensity to a useful level), was positioned in the sample compartment similar to an ordinary cuvette. The pinhole was aligned with the emission slit, selected to give the narrowest instrumental bandwidth, 1 nm. The slit near the photomultiplier was adjusted similarly. The wavelength dials were exposed by removing the instrument cover, and the orientation of the wavelength dial with respect to the drive shaft could be adjusted after loosening several screws. The dial was thus adjusted manually to give the closest correspondence with the reference mercury lines, as observed on a meter associated with the photometer.

Wavelength calibration of the excitation monochromator was done in a similar fashion. The excitation bandwidths were adjusted to 1 nm and the standard (xenon) lamp housing was removed. The mercury lamp, in a similar housing with a large slot, was placed near the external slit. A special cell having a thick layer of barium sulfate (white reflector) was placed at the sample location and served to diffuse the dispersed mercury light before entry into the emission monochromator. The emission monochromator was tuned to pass zero order light, so that the mercury lines were not re-dispersed. The excitation monochromator dial was adjusted manually as described previously for the emission dial.

An almost linear relation was noted between the dial wavelengths and the mercury wavelengths between 250 and 580 nm. Therefore, a linear regression analysis was performed to determine the least squares slope and intercept for both wavelength dials. These coefficients were stored in the 1130 computer and used to correct the values read from the dials.

These calibrations were repeated at intervals of 30-60 days to compensate for small drifts in the calibration; these were probably caused by wear of the wavelength cam. The wavelength calibration is accurate to $\pm$1 nm.

The other fluorimeter calibration involved a determination of the relative spectral responsivity of the emission monochromator. This "emission calibration" combines effects of optical efficiencies (mirrors and grating) and photomultiplier response as a function of wavelength. This calibration involves a measurement of the instrumental response to a source (or sources) of known relative spectral irradiance. The source(s) could be either materials whose emission spectra have been accurately corrected, or could be light sources of known relative spectral irradiance. In the present work, calibrated sources were used so that a wide spectral region could be covered easily, and the reference data was of greater accuracy. The source used in this work was a 200 watt tungsten-halogen lamp, electrically and geometrically equivalent to a type calibrated by the National Bureau of Standards(30). This lamp was positioned about 70 cm from the fluorimeter compartment and operated at the stated current (6.5 amps AC). The lamp current was adjusted by use of an autotransformer, which appeared to give good regulation; better stability could be achieved by operating the transformer from a constant voltage transformer.

An aluminum block containing a heavy layer of barium sulfate was placed in the sample compartment and served to diffuse the light before entry into the emission monochromator.

The tungsten-halogen lamp spectrum was digitized at approximately 2 nm intervals between 250 and 750 nm. This curve was divided by the known relative irradiance values (30) using linear interpolation to estimate values at wavelengths not covered in the reference data. The calibration curve obtained in this fashion was mainly featureless, but exhibited a sharp rise below about 300 nm. This rise is an artifact, probably due to increasing contribution of zero order light relative to the (much weaker) lamp intensity in this region. For this reason, this particular lamp is not well-suited for calibration at short wavelengths. In order to obtain calibration data at short wavelengths, the normal xenon lamp spectrum

was used. This "excitation calibration" was achieved by use of a concentrated rhodamine B solution (10 gm/liter in ethylene glycol), which functions as a quantum counter over the 250-600 nm region (31). This solution was contained in a triangular cell, and the rhodamine emission was monitored at 640 nm. To complete the calibration measurement, the excitation and emission monochromators were synchronously scanned at the same wavelength, with the barium sulfate cell serving as a diffusing surface. Division of this latter curve by that obtained from rhodamine yielded the desired calibration curve. The complete emission calibration curve was obtained by joining this curve to that obtained from the tungsten halogen lamp at about 350 nm.

As a check of the calibration, corrected spectra of anthracene in ethanol were obtained, the relative vibronic intensities compared with those available in the literature. These values (units of quanta per wavelength internal) are summarized in Table 5; wavelengths are approximate.

TABLE 5. COMPARISON OF RELATIVE VIBRONIC INTENSITIES OF ANTHRACENE IN ETHANOL

λ(nm)	Ref. 10	Ref. 32	Ref. 6	This Work
380	1.00	1.00	1.00	1.00
400	1.04	1.04	0.97	0.995
420	0.46	0.49	0.48	0.491
450	0.14	0.14	0.15	0.141

In general, the data obtained here is within 10% of that obtained by other workers. Differences from one laboratory to another are most probably a result of errors in instrument calibration.

A similar comparison of relative vibronic intensities for benzene and fluoranthene is summarized in Table 6 below.

TABLE 6. RELATIVE VIBRONIC INTENSITIES OF BENZENE AND FLUORANTHENE

Benzene			Fluoranthene		
λ(nm)	Ref. 5	This Work	λ(nm)	Ref. 10	This Work
270	0.73	0.76	410	0.20	0.24
278	1.00	1.00	420	0.30	0.35
285	0.73	0.79	440	0.75	0.82
295	0.40	0.51	465	1.00	1.00
			495	0.65	0.74
			570	0.20	0.16

It should be noted that the benzene spectrum in Ref. 5, also obtained in cyclohexane solvent, was approximately 30 times more concentrated, so that distortions due to reabsorption may exist. The fluoranthene spectrum of Ref. 10 was in ethanol, whereas the spectrum here was in cyclohexane. Despite these differences, the overall agreement is satisfactory.

In order to obtain a more direct estimate of the accuracy of the calibration, the irradiance of the tungsten-halogen lamp between 270 and 700 nm was determined using a calibrated spectroradiometer. Although absolute values were lower than those of Ref. 10, the relative values agreed within ±10% above 300 nm. Below 300 nm, the lamp output is quite low, and the estimated uncertainty is approximately ±15%.

In summary, the emission calibration should be accurate to ±10% between 300 and 700 nm, but may be less accurate (±15%) below 300 nm.

3.4 Data Reduction

Spectral data was obtained on 109 compounds. If no detectable fluorescence was observed, an alternate compound was used. Information contained in the fluorescence spectra is tabluated in Section 4. The data includes the code letters, excitation wavelength, wavelength of maximum emission, number of peaks, number of shoulders, width at half maximum and detection limits. Most of these parameters were used in the spectral code which is described below.

3.4.1 Detection Limits

The detection limit for the fluorescing material has been defined as the concentration at which the signal-to-noise ratio (S/N) at the fluorescence maximum is equal to two.

It should be noted that other techniques have been used to define detection limits. Hirschfield (40-42) chooses to use integral rather than peak ratios.

In practice, the stock solutions were serially diluted by factors of ten until the fluorescence signal became near or slightly below the detection limit. Signal-to-noise ratios were calculated for the two samples of lowest concentration, and the values linearly extrapolated to the concentration corresponding to the S/N of two.

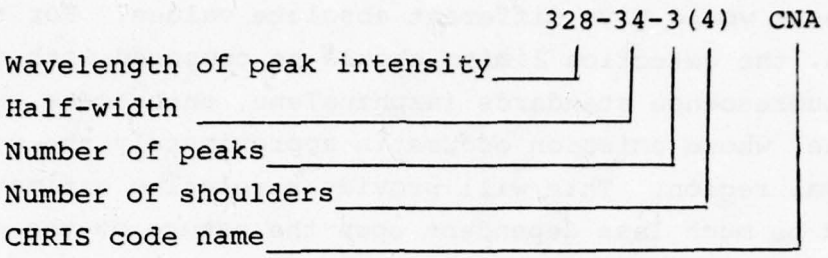
In some cases, solvent background in the form of impurity emission or Raman peaks in the vicinity of the sample fluorescence resulted in greater uncertainty. In addition, certain compounds showed photochemical instability. For these cases, the detection limits must be regarded as approximate.

The units of concentration are given nominally in parts per million, although they are actually in units of mg/l. It should

emphasized that these values are dependent upon the characteristics of the instrumentation (light intensity, optical efficiency, and detector sensitivity) and thus, different equipment would give different absolute values. For this reason, the detection limits should be compared with one of the fluorescence standards (naphthalene, anthracene, and fluoranthene) whose emission occurs in approximately the same spectral region. This will provide a relative estimate which should be much less dependent upon the nature of the equipment.

3.4.2 Spectral Code

In establishing a spectral code, certain features of the fluorescence spectra must be selected for quantitation. Although the choice of these features is somewhat arbitrary, they should summarize the important spectral features and yet permit a non-specialist to construct an equivalent code for an unknown material. The following spectral parameters have been selected to be included in the code: wavelength at peak maximum, width at half maximum, number of distinct peaks, and the number of shoulders. The last two parameters sometimes constitute a "gray" area in that one observer may classify a peak as a shoulder (or conversely) and another observer may argue about the existence of a shoulder. For this contract, each spectrum of a toxic or hazardous material was examined by several people in an attempt to determine the code. Shoulders were chosen if they were not resolved as a peak from the peak in the spectrum. Certain materials (such as, the polynuclear aromatic hydrocarbons) have highly structured spectra, in which case measurement of half width is difficult to obtain. In cases of highly structured spectra, the half-width measurement was made based on the highest peak in the spectrum. For weakly or non-emitting compounds, the half-width measurements are denoted by N because of the difficulty and inaccuracy in measuring them. A typical code is illustrated below for N 1-Chloronaphthalene.



In the list of coded spectra, the entries are organized in order of increasing peak wavelength, so that this parameter functions as the primary identifier. The corresponding spectra are grouped alphabetically according to their CHRIS list code name.

The present code structure should be regarded as preliminary in nature, in that other spectral features or some algebraic combination of parameters might serve as more useful identifiers.

4. INTERPRETATION

4.1 Introduction

It was the purpose of this contract to investigate the fluorescence properties of one hundred toxic and hazardous materials and produce corrected emission curves and derive a spectral code for these materials. One hundred twenty-five potential compounds were selected based on structural and known properties for study, and of these, one hundred thirteen were received and studied.

Fluorescence spectroscopy is well regarded as an analytical tool because of its excellent sensitivity and added selectivity compared to other methods. An attempt has been made in this contract to examine the use of fluorescence for identification and quantitation of toxic and hazardous materials. There have been many studies which have examined the relationship between molecular structure and fluorescence and a number of generalities exist. A great majority of organic compounds which exhibit analytically useful fluorescence possess cyclic conjugated structures. The fact that a molecule possesses these structural characteristics however, does not guarantee that the species will fluoresce. The reverse is also true. The shape of the fluorescence spectrum, its position as a function of wavelength, and the intensity of the luminescence are sensitive to molecular structure, symmetry and the environment in which the molecule finds itself. Of the 113 materials supplied by the United States Coast Guard 96 compounds were fluorescent at room temperature, some very weakly however. Thirteen compounds were considered non-fluorescent at room temperature. The spectra of these compounds show little or no difference from the solvent background. The spectrum and solvent background for some of these thirteen materials can be found in the compendium. No digitized data was obtained for Diazinon, dimethylterephthalate, 2,4-dinitroaniline, 4,6-dinitro-o-cresol and m-nitroaniline. These materials were determined to be non-fluorescent from preliminary scans on the fluorimeter. Four compounds on the original list were not run. Table 7 summarizes these results. A complete table of experimental parameters and detection limits can be found at the end of this section (Table 13).

TABLE 7. SUMMARY OF FLUORESCENT TOXIC AND HAZARDOUS MATERIALS

Fluorescent	Non-Fluorescent	Not Run
acenaphthene	atrazine	anisoylchloride
acetone	benzoylchloride	methylene diphenylene-isocyanate
acridine	butylbenzylphthalate	
aniline	Diazinon	Nitralin
anthracene	Dichlone	Trifluralin
Aroclor 1242	dimethylterephthalate	
Aroclor 1254	2,4-dinitroaniline	
azinphosmethyl	4,6-dinitro-o-cresol	
benzanthracene	2,4-dinitrophenol	
benzene	diphenylhydrazine	
benzonitrile	m-nitroaniline	
benzo(a)pyrene	Parathion	
benzyl alcohol	piperazine	
benzylamine		
benzyltriethylammon-iumchloride		
Bisphenol A		
brucine		
o-tert-butylphenol		
p-tert-butylphenol		
carbaryl		
carnauba wax		
castor oil		
catechol		
p-chloroaniline		
1-chloronaphthalene		
p-chlorophenol		
chloropyrifos		
4-chloro-o-toluidine		
p-chlorotoluene		
chrysene		
coconut oil		

TABLE 7. SUMMARY OF FLUORESCENT TOXIC AND HAZARDOUS MATERIALS (con't.)

Fluorescent
cod liver oil
copper naphthenate
cottonseed oil
Coumaphos
o-cresol
p-cresol
cumene
p-cymene
DDD
DDT
1,2,5,6-dibenzanthracene
Dicamba
Dichlorobenil
dichlorophenoxyacetic acid
dichlorodiphenylsilane
diethylbenzene
diethylene glycol
diethylphthalate
2,4-dimethylphenol
3,5-dimethylphenol
dinitrophenol
diphenylamine
diphenylether
diquat dibromide
dodecylbenzene
Dowtherm
ethylbenzene
fluoranthene
gallic acid
hydroquinone
indene
lard
linseed oil
methyl isobutyl ketone
α-methylstyrene

TABLE 7. SUMMARY OF FLUORESCENT TOXIC AND HAZARDOUS MATERIALS (con't)

Fluorescent
methoxychlor
n-methylaniline
naphthalene
α-naphthylamine
nonylphenol
olive oil
palm oil
peanut oil
phenol
phthalic acid
polyethoxylated nonylphenol
pyrogallic acid
quinoline
resorcinol
salicylic acid
sodium dodecylbenzene sulfonate
styrene
tannic acid
tetrahydronaphthalene
toluene
p-toluene sulfonic acid
p-toluidine
tricresyl phosphate
1,3,5-triethylbenzene
turpentine
undecylbenzene
uranyl nitrate
m-xylene
o-xylene
zirconium acetate

Compounds were considered fluorescent if they exhibited a reproducible signal above the solvent background spectrum. In some cases (i.e., methyl isobutyl ketone) the fluorescence is extremely weak but consistent with what is found in the literature for a compound of similar structure (i.e., acetone).

4.2 Spectral Similarities and Interferences

4.2.1 Use of Absorption Spectra

In order to insure the integrity of the chemicals received, the absorption spectra of all the toxic and hazardous materials supplied were run. Not only did these spectra help in locating the proper wavelength for excitation but were used for comparison with literature spectra for detecting the presence of impurities. Only one compound, p-cymene showed no resemblance to the published Sadtler absorption spectrum. Four compounds (acridine, dodecylbenzene, quinoline and undecylbenzene) whose absorption spectra agreed with published work showed fluorescent impurities. The concentration of these impurities was either too low for identification using the absorption spectra or it overlapped with the primary compound absorption. For all other compounds where absorption spectra were available in the literature the agreement was very good.

4.2.2 Comparison of Available Fluorescence Spectra

It is difficult to compare the data obtained in this contract with most spectra appearing in the literature, since most of these are uncorrected. For example, an attempt was made to compare our spectra with those published by Sadtler, but there were many discrepancies. This is because uncorrected emission spectra reflect instrumental factors such as monochromator efficiency and detector response as a function of wavelength. Uncorrected excitation spectra, although not obtained under this contract, would be modulated by the spectral intensity

distribution of the light source. These instrumental factors introduce changes in wavelength and relative intensity into the spectra, making comparisons difficult. Although small differences among corrected spectra may exist due to calibration methods used, these will generally be minor in comparison with uncorrected data.

There are several advantages to using corrected data. The first is that spectra obtained on totally different instruments are more easily compared. Another is that accurate quantum yield measurements, which provide a measure of fluorescence intensity, require corrected data. Calibration of certain other spectral parameters, such as radiative lifetimes (related to fluorescence decay times) also require corrected spectral data.

In Section 3 of this report, comparisons of corrected fluorescence intensities in the literature with the data obtained for this contract for anthracene, benzene and fluoranthene were given. Below are tabulated results for other compounds for which corrected data exists. In most cases the agreement is good.

TABLE 8. COMPARISON OF CORRECTED RELATIVE FLUORESCENCE INTENSITIES

Chrysene	This Work	Ref. 10	Ref. 5
363	1.00	1.00	1.00
383	1.044	.975	1.16
404	.464	.425	.553
428	.125	.100	.160
Benz(a)pyrene			
405	1.00	1.00	
428	.500	.506	
455	.123	.152	

TABLE 8. COMPARISON OF CORRECTED RELATIVE FLUORESCENCE INTENSITIES (con't)

1,2,5,6 Dibenzanthracene	This Work	Ref. 5
396	1.00	1.00
418	.564	.480
442	.171	.133
Acenaphthene		
323	1.00	.978
328	.526	.615
338	.780	1.00
355	.289	.363
Benzene		
271	.76	.692
279	1.00	1.00
286	.794	.75
Benzylalcohol		
278	.817	.797
284	1.00	1.00
Ethylbenzene		
278	.943	.874
283	1.00	1.00
Naphthalene		
323	1.00	1.00
337	.879	.923

TABLE 8. COMPARISON OF CORRECTED RELATIVE FLUORESCENCE INTENSITIES (con't)

Styrene	This Work	Ref. 5
294	.931	.849
303	1.00	1.00
Toluene		
278	.98	.890
284	1.00	1.00

4.2.3 General Comments on Samples

In general there were very few problems involved in running the samples of toxic and hazardous materials as previously mentioned. For a few samples there were problems of impurity emission and photochemical changes upon emission. Also, in several cases there was a change in the emission spectrum when the solvent was changed from cyclohexane to ethanol or some other specified solvent.

Acridine was prepared in both cyclohexane and ethanol. For both excitation wavelengths, 290 nm and 355 nm, the acridine emission was much stronger in ethanol. Impurity emission, however, was present when acridine was run in both solvents. A quick recrystallization of the acridine from ethanol did not produce any significant change. Acridine also showed photochemical decomposition.

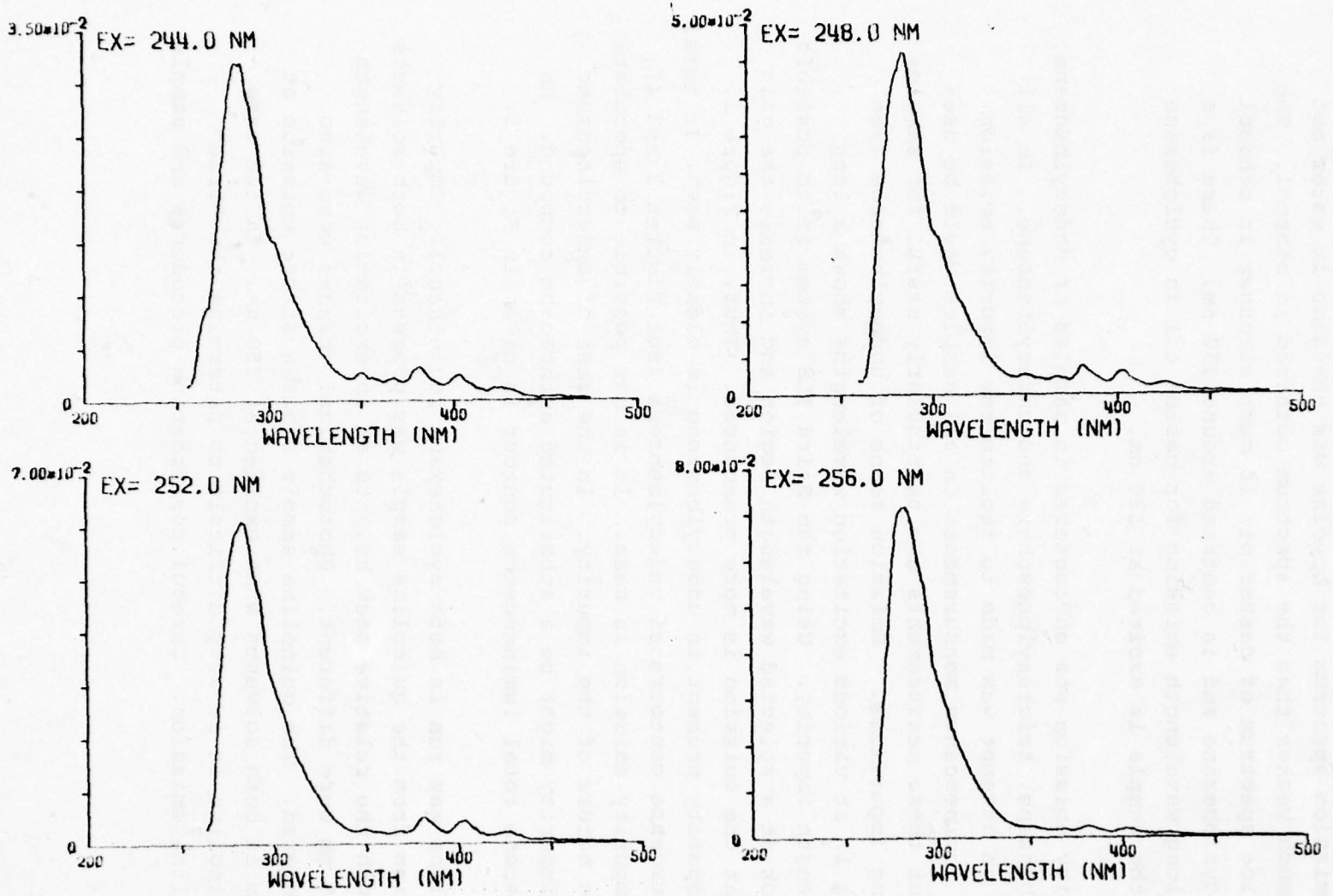
Azinphosmethyl was run in both cyclohexane and ethanol. There was little solvent dependence on the emission intensity and the emission maximum was entered around 430 nm in both solvents. Brucine was originally run in ethanol. However, the terms of the contract called for running the sample in water first.

The emission spectrum for brucine was the same in water but very much weaker than the spectrum obtained in ethanol. The emission spectrum of castor oil is much stronger in ethanol than cyclohexane and is centered around 330 nm. There is a weak long wavelength emission for castor oil in cyclohexane when the sample is excited at 320 nm.

Impurity emission was encountered in samples of dodecylbenzene, ethylbenzene, tricresylphosphate and undecylbenzene. In all cases an attempt was made to isolate the impurity emission. Total luminescence measurements on all samples would be useful but these measurements are particularly useful for samples showing impurities. Emission scans of undecylbenzene (see Figure 1) at various excitation wavelengths shows a long wavelength impurity. Using the Baird TLS system it is possible to look at a selected wavelength region and increase the gain so that the emission is more pronounced. Thus, in Figure 2, the impurity present in undecylbenzene is clearly seen. In total luminescence contours of undecylbenzene (see Figures 3 and 4), the impurity emission is seen. It is now possible to speculate on the nature of the impurity. In the case of undecylbenzene this impurity might be a substituted anthracene compound. An anthracene total luminescence contour is given in Figure 5.

Quinoline was run in both cyclohexane and ethanol. Impurity emission from the quinoline sample was present in both solvents although the relative peak heights at an excitation wavelength of 275 nm were different. Photochemical changes were also encountered. The quinoline sample shows a strong emission at 430 nm in both solvents when excited at 350 nm. In the case of quinoline it is very difficult to determine the "true" quinoline emission. Careful purification procedures and sample

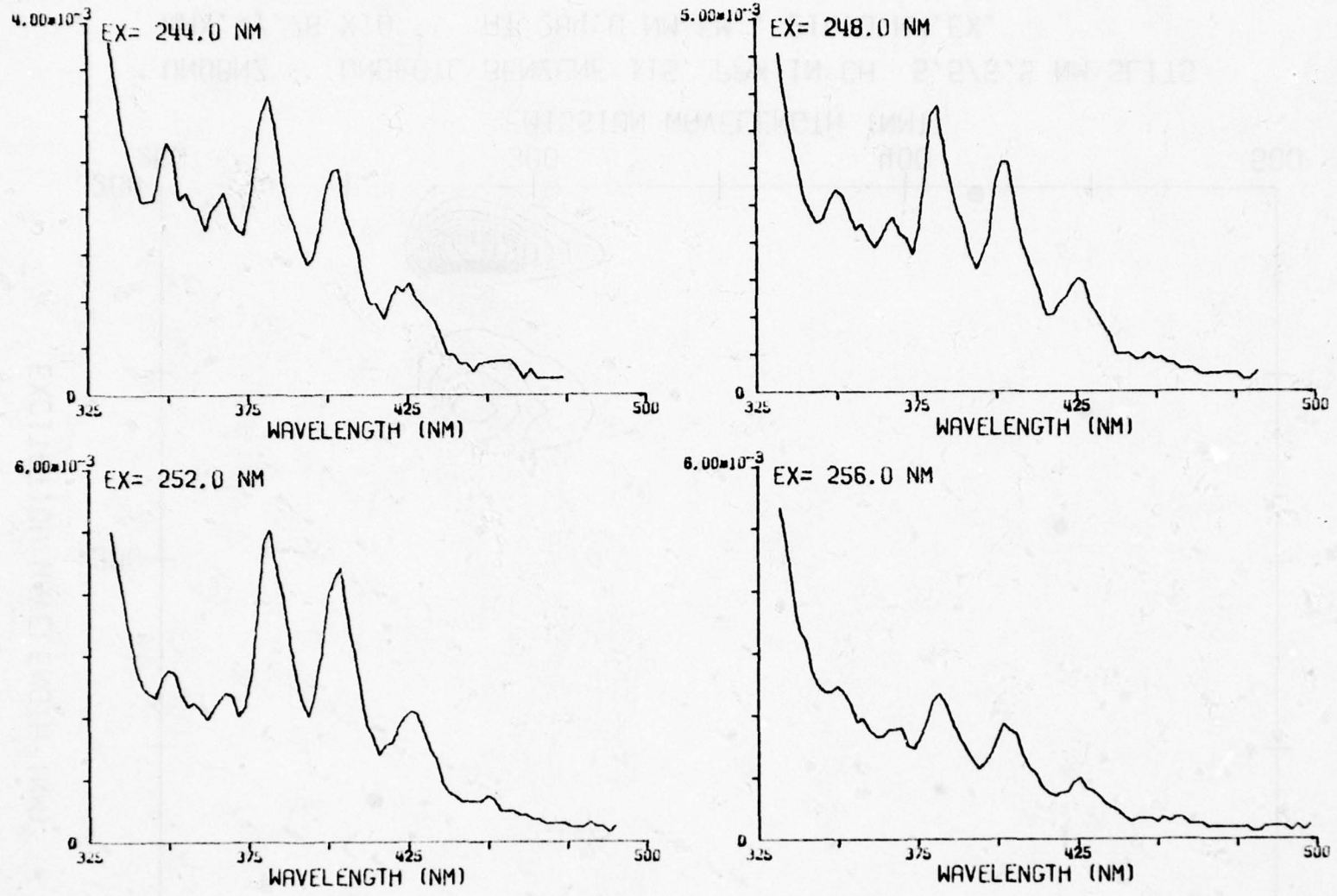
5 /9 /79



UNDBNZ UNDECYL BENZENE 115. PPM IN CH 5,5/5,5 NM SLITS

FIGURE 1

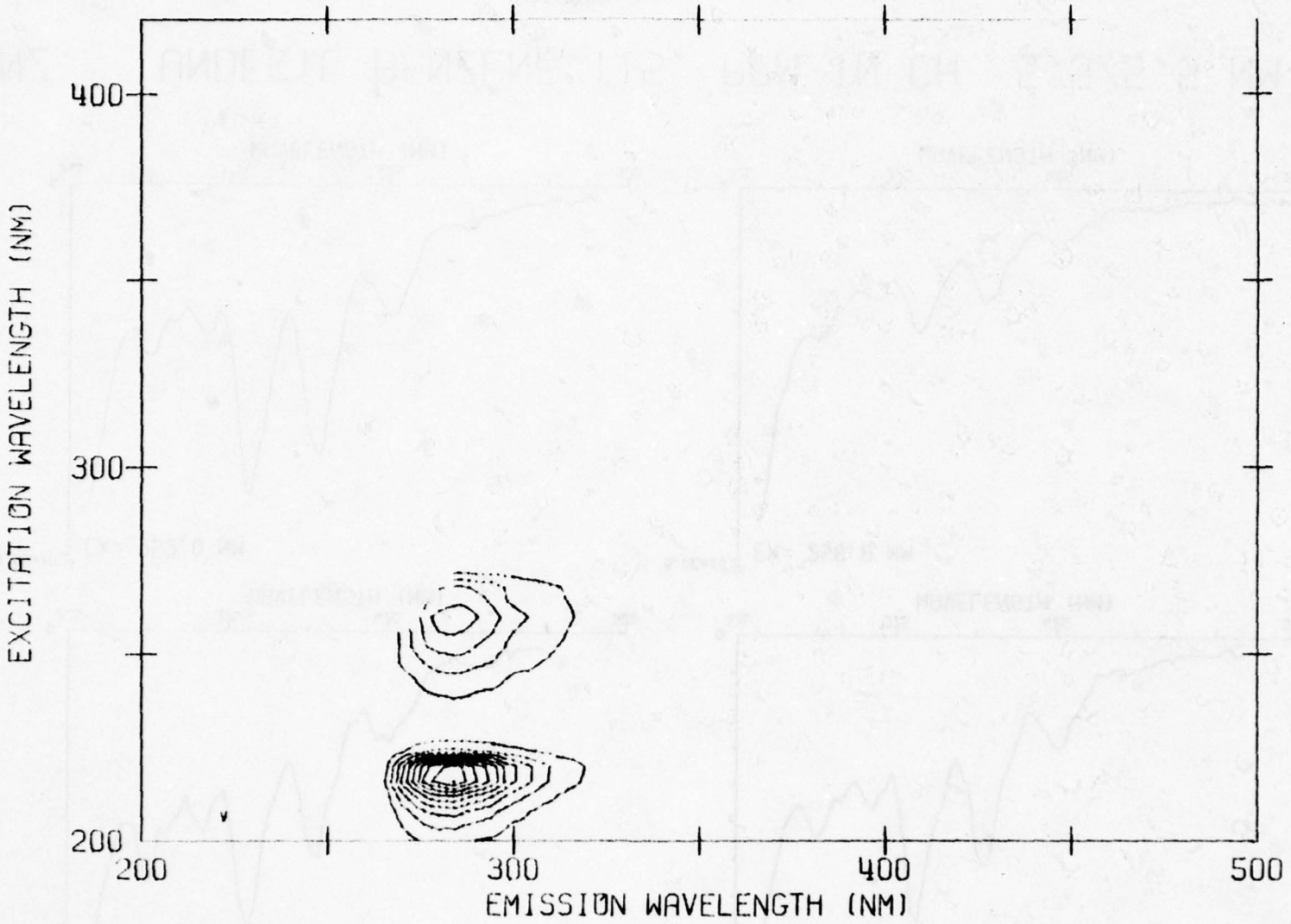
5 /9 /79



UNDBNZ UNDECYL BENZENE 115. PPM IN CH 5,5/5,5 NM SLITS

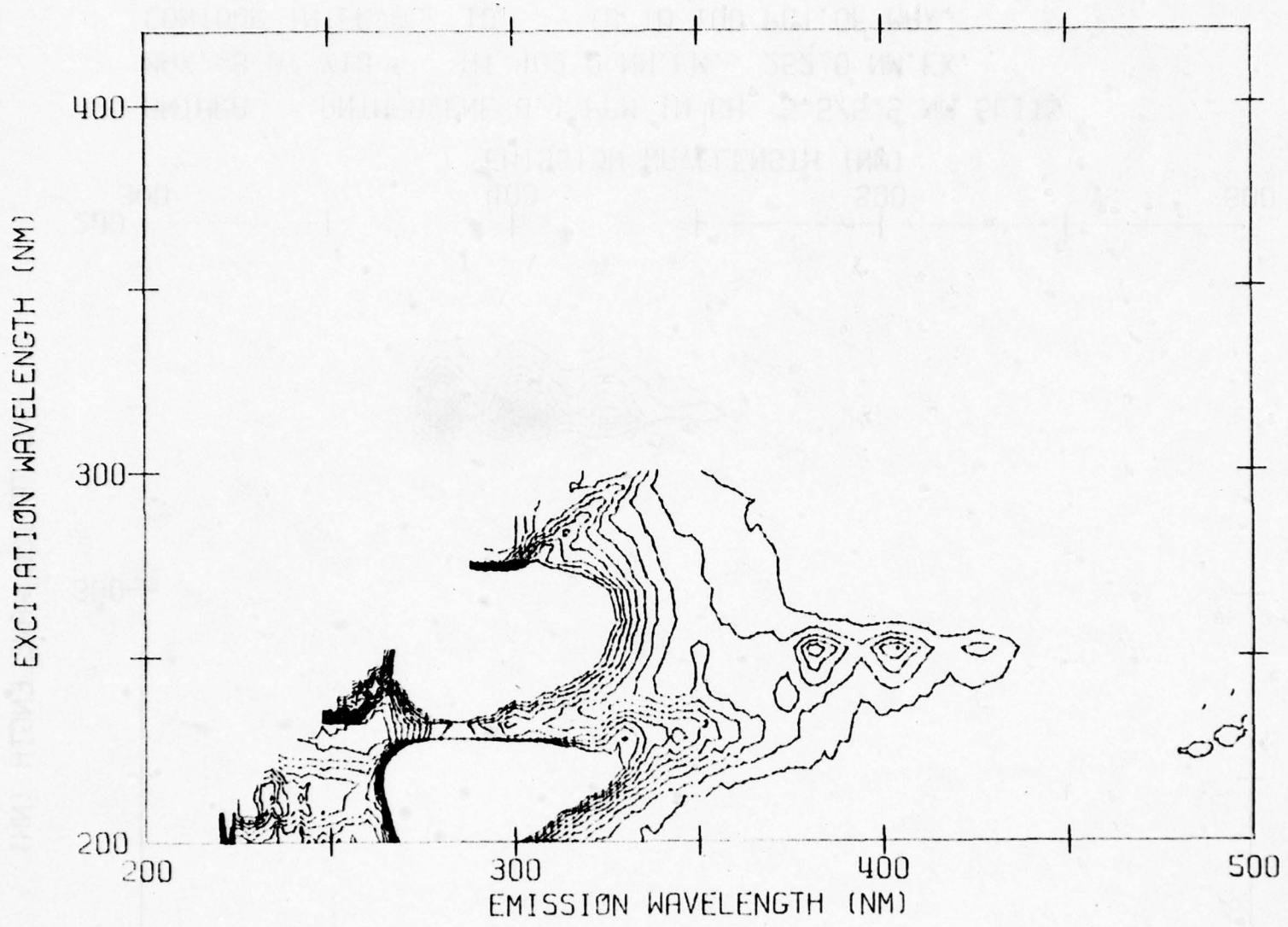
FIGURE 2

5 /9 /79



UNDBNZ UNDECYL BENZENE 115. PPM IN CH 5,5/5,5 NM SLITS
MAX.=1.76 X10^{-1} AT 284.0 NM.EM., 216.0 NM.EX.
CONTOUR INTERVAL= 10 10 TO 100 PCT.OF MAX.

FIGURE 3

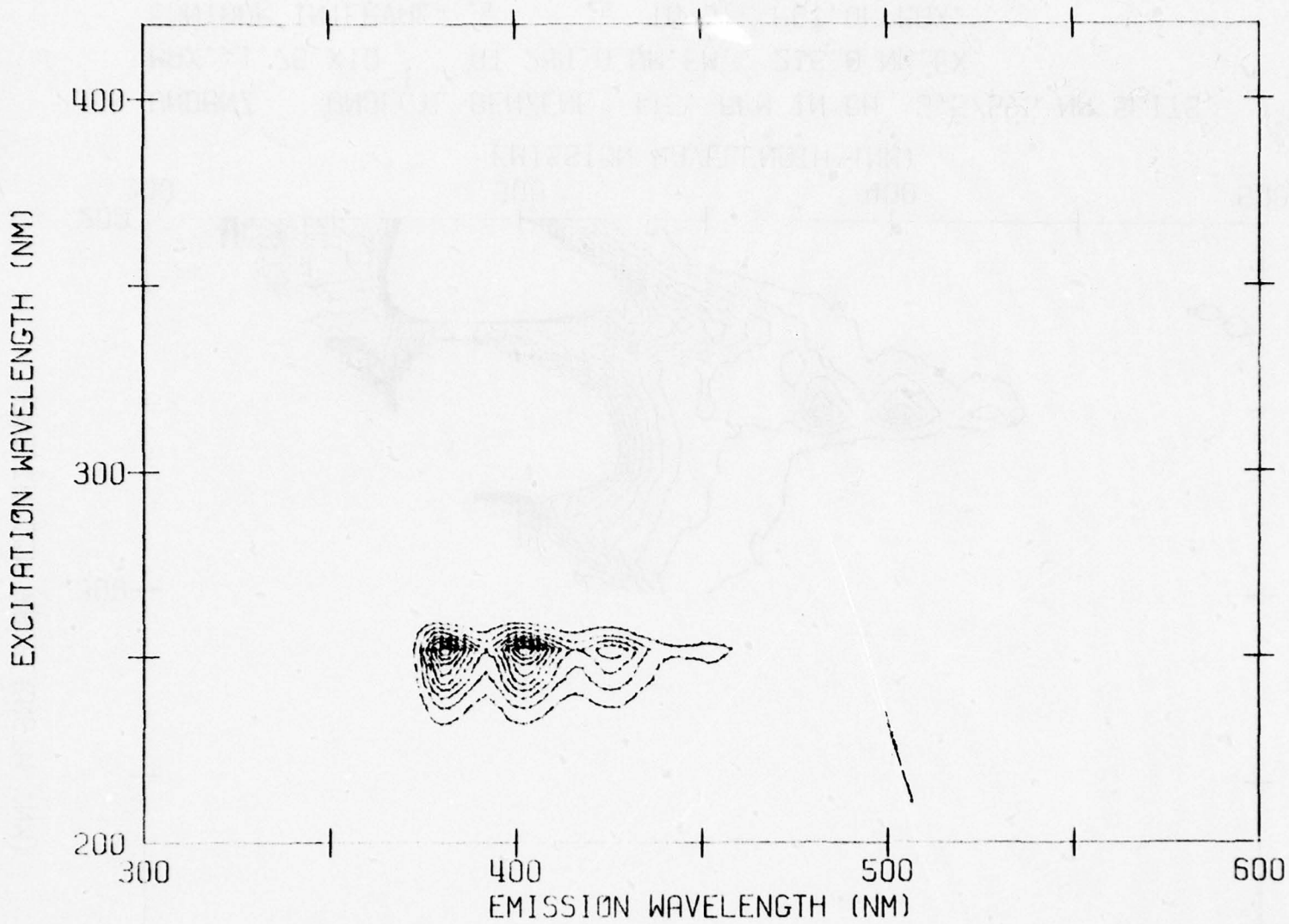


UNDBNZ UNDECYL BENZENE 115. PPM IN CH 5,5/5,5 NM SLITS

MAX.=1.76 X10^{-1} AT 284.0 NM.EM., 216.0 NM.EX.

CONTOUR INTERVAL= .5 .5 TO 5 PCT.OF MAX.

FIGURE 4



ANTHRA ANTHRACENE 0.1 PPM IN CH 5,5/5,5 NM SLITS
MAX.=8.07 X10^{-1} AT 402.0 NM.EM., 252.0 NM.EX.
CONTOUR INTERVAL= 10 10 TO 100 PCT.OF MAX.

FIGURE 5

handling techniques (nitrogen atmosphere) are necessary to obtain the correct spectrum for quinoline.

In addition to acridine and quinoline photochemical changes were encountered with diphenylamine, Dicamba and the Aroclor mixtures. This made the determination of a detection limit difficult in some cases. Those compounds on the Chris and EPA lists which undergo photochemical changes require further study if the photoproduct(s) are to be identified.

Zirconium acetate was insoluble in all the solvents used which included cyclohexane, water, ethanol and acetonitrile. It was soluble in a 1.0 M H_2SO_4 solution. The fluorescence spectrum of a 216 ppm sample and solvent background are given in Figures 6 and 7. The fluorescence is very weak. No detection limits were determined for this sample.

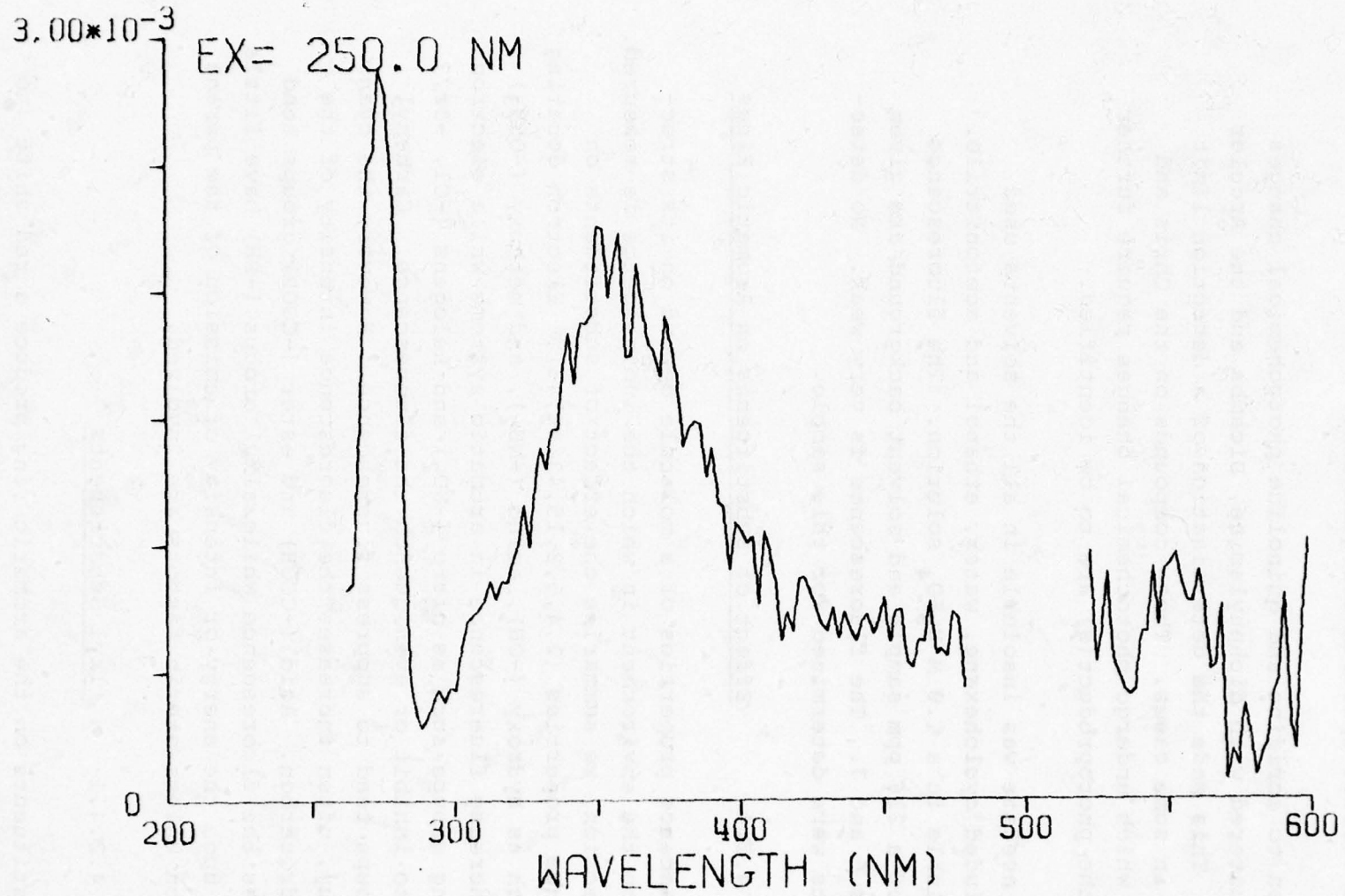
4.2.4 Effect of Substituents on Aromatic Rings

The luminescence properties of a molecule depend on its structure and on the environment in which the luminescence is measured. In this section, we summarize the effect of substituents on fluorescence properties (2,4,5,8,15,43,44,45). Electron donating groups such as hydroxy (-OH), amino ($-NH_2$), and methoxy ($-OCH_3$) tend to increase fluorescence in aromatic systems while electron withdrawing groups such as nitro ($-NO_2$) and halogens (-Cl, -Br, -I) tend to inhibit or even quench the fluorescence. Carbonyl (>C=O) groups tend to suppress fluorescence. However, the cyano (-CN) group, often increases the fluorescence intensity of the parent hydrocarbon. Acid (-COOH) and ester (-COOR) groups tend to suppress the fluorescence while alkyl groups (-RH) have little influence upon the energy or intensity of emission of the parent hydrocarbon unless steric factors are involved.

4.2.4.1 Alkyl Substituents

Alkyl substituents on the aromatic ring produce a red shift (to longer wavelengths) in both absorption and fluorescence(2,4,5,8,).

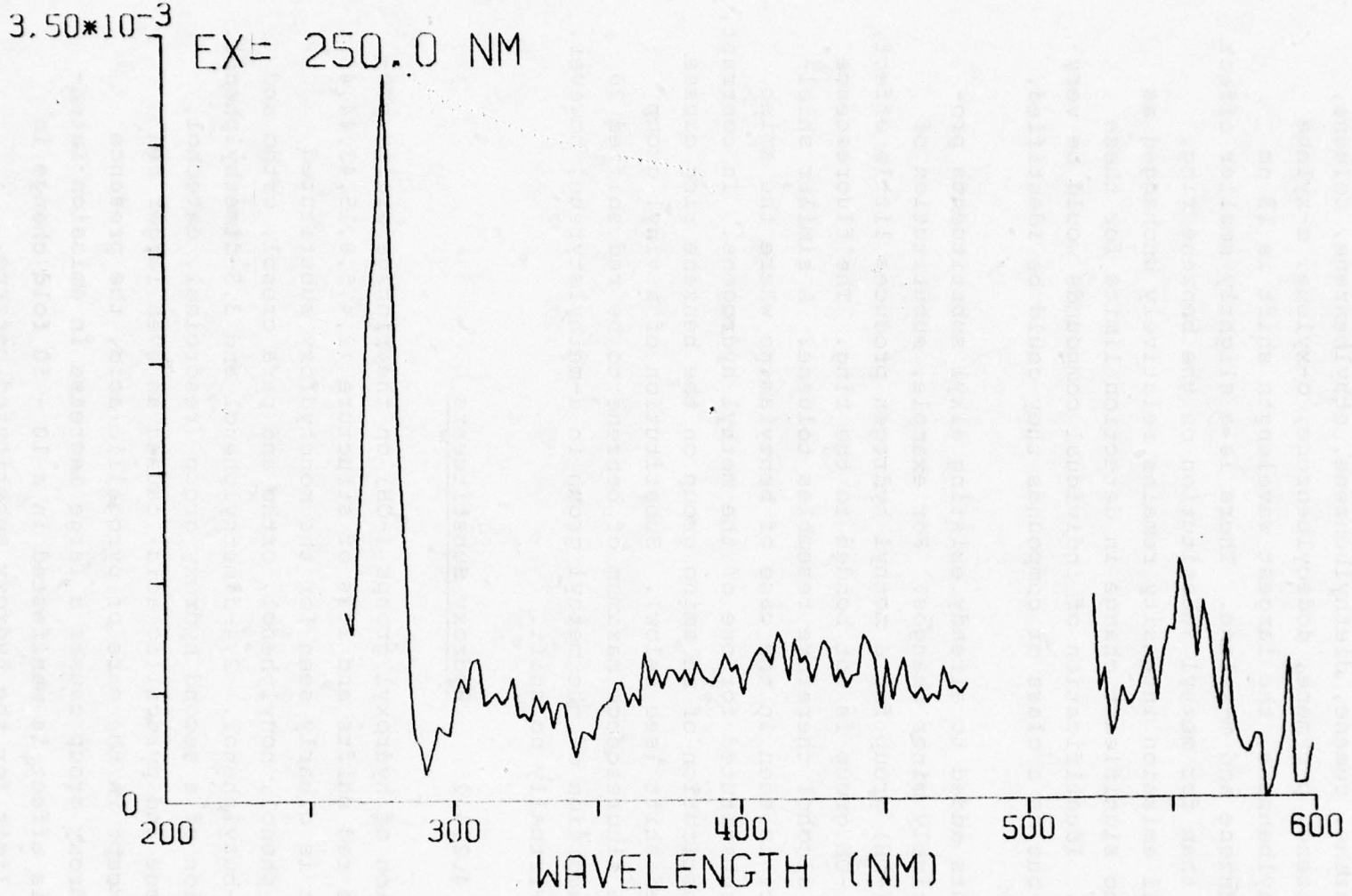
5 /8 /79



ZIRCONIUM ACETATE IN 1.M H2S04 10,10/2,2 NM SLITS

FIGURE 6

5 /8 /79



1.M SULFURIC ACID 10,10/2,2 NM SLITS

FIGURE 7

For the alkyl-substituted benzenes studied under this contract, namely benzene, cumene, diethylbenzene, ethylbenzene, toluene, undecylbenzene, p-cymene, dodecylbenzene, o-xylene, m-xylene and triethylbenzene, the largest wavelength shift is 15 nm between benzene and m-xylene. There is a slightly smaller effect for ethyl than for methyl substitution on the benzene ring. The overall emission intensity remains relatively unchanged as there is no significant change in detection limits for these compounds. Identification of individual compounds would be very difficult but as a class of compounds they could be identified.

Substituents added to already existing alkyl substituents produce relatively minor changes. For example, substitution of hydroxyl (-OH) group for a methyl hydrogen produces little effect, since the -OH group is not bonded to the ring. The fluorescence of benzyl alcohol therefore resembles toluene. A similar shielding effect is seen in the case of benzylamine where the amino group is substituted for one of the methyl hydrogens. In contrast, direct substitution of an amino group on the benzene ring causes a large red shift (see below). Substitution of a vinyl group causes the fluorescence maximum of benzene to be red shifted 20 nm. The addition of the methyl group in α-methylstyrene, however, produces virtually no shift.

4.2.4.2 Hydroxy Substituents

Substitution of hydroxyl groups (-OH) on the ring generally produce large red shifts and loss of structure (2,4,5,8,15,43,44,45). This shift is clearly seen for the monohydroxy substituted benzenes; phenol, nonylphenol, ortho and para cresol, ortho and para-tert-butylphenol, 2,4-dimethylphenol and 3,5-dimethylphenol. Substitution of a second hydroxy group (resorcinol, catechol, hydroquinone and pyrogallic acid) causes an even larger red shift. Except in the case of pyrogallic acid, the presence of the hydroxy group causes a large increase in emission intensity. This effect is manifested in a 10 - 50 fold change in detection limit for the hydroxy substituted benzene.

4.2.4.3 Amino Substituents

Substitution of the amino ($-NH_2$) group for hydrogen on the benzene rings results in a large red shift, an increase in emission intensity and a loss of structure in the fluorescence spectrum (2,4,5,8,15,43,44,45). These effects are clearly demonstrated in benzene/aniline and naphthalene/α-naphthylamine. The peak emission is shifted from 279 nm to 316 nm for benzene/aniline and from 323 nm to 377 nm for naphthalene/α-naphthylamine. In both cases the structure of the unsubstituted compound is lost with the addition of the amino group but the detection limit is improved by a factor of 50 to 100. The effect of added substituents after the initial amino group is quite small. There is no significant wavelength shift or change in the fluorescence yield for methylaniline, p-toluidine, p-chloroaniline and 4-chloro-o-toluidine.

4.2.4.4 Cyano Substituents

Benzonitrile, with its electron releasing cyano (-CN) group is only slightly shifted to longer wavelength compared to benzene (2,4,5,8,15,43,44,45). The cyano group results in an increase in emission intensity and this can be seen in the factor of 10 lower detection limit for benzonitrile compared to benzene.

4.2.4.5 Nitro Substituents

Nitro ($-NO_2$) groups tend to totally quench the fluorescence of aromatic hydrocarbons (2,4,5,8,15,43,44,45). No fluorescence emission was observed for 2,4-dinitroaniline, m-nitroaniline, 4,6-dinitro-cresol and 2,4-dinitrophenol. At 77°K in methylcyclohexane and ethanol, p-nitrophenol and p-nitroaniline do not exhibit fluorescence but do show phosphorescence in each solvent with the ethanol spectrum being red shifted from that of methylcyclohexane (33). Nitrobenzene, p-nitrotoluene, p-chloro-nitrobenzene and p-nitroanisole have a lowest triplet ($n-\pi^*$) state but do not exhibit phosphorescence at low temperature. The

reason for this is not understood. Heavy atom effects and predissociation have been used to explain the fluorescence quenching of nitro substituted aromatic compounds.

4.2.4.6 Halogen Substituents

There are only a few examples of halo-substituted compounds (X=F, Cl, Br, I) in this contract. Direct substitution of a halogen increases the rate of intersystem crossing due to the internal heavy atom effect, resulting in a reduction in the fluorescence efficiency (2,4,5,8,15,43,44,45). In addition to this decrease in fluorescence intensity there is a shift to longer wavelength. The effect is not as great for toluene and p-chlorotoluene, λmax = 284 nm and λmax = 288 nm, respectively. A more dramatic shift in wavelength can be seen for phenol and p-chlorophenol, λmax = 288 and λmax = 305 nm respectively.

4.2.4.7 Acid and Acid Chloride Substituents

Acid substituents (-COOH) and acid chlorides (-COOCl) result in a decrease in emission frequency and a large decrease in emission intensity(2,4,5,8,15,43,44,45). The simplest acid substituted benzene derivative, benzoic acid, does not fluoresce at room temperature (5). The lack of fluorescence of benzoic acid in solution is attributed to the fact that the lowest excited state is n,π^* in character. The presence of the acid group deactivates the benzene ring by withdrawing π electrons and reducing their mobility. At low temperature a very weak fluorescence is observed. All of the benzene substituted carboxylic acids (except phthalic acid) studied under this contract had other substituents attached to the benzene ring. This altered the fluorescence characteristics of the molecule. Phthalic acid, a benzene dicarboxylic acid, exhibited a weak fluorescence with

an emission maximum some 60 nm shifted to the red of benzene. The fact that benzoic acid does not fluoresce at room temperature coupled with the presence of the second acid group suggests that the observed luminescence may be due to an impurity. Room temperature phosphorescence on silica gel has been reported recently by Hurtubise(34). Addition of hydroxy groups to the benzene carboxylic acid structure counteracts the effect of the acid. If intramolecular hydrogen bonding occurs between substituents this may modify the fluorescence. Hydrogen bonding with other phenolic hydroxy substituents may be the reason salicyclic, gallic and tannic acid all exhibit enhanced fluorescence emission which is red shifted from benzene.

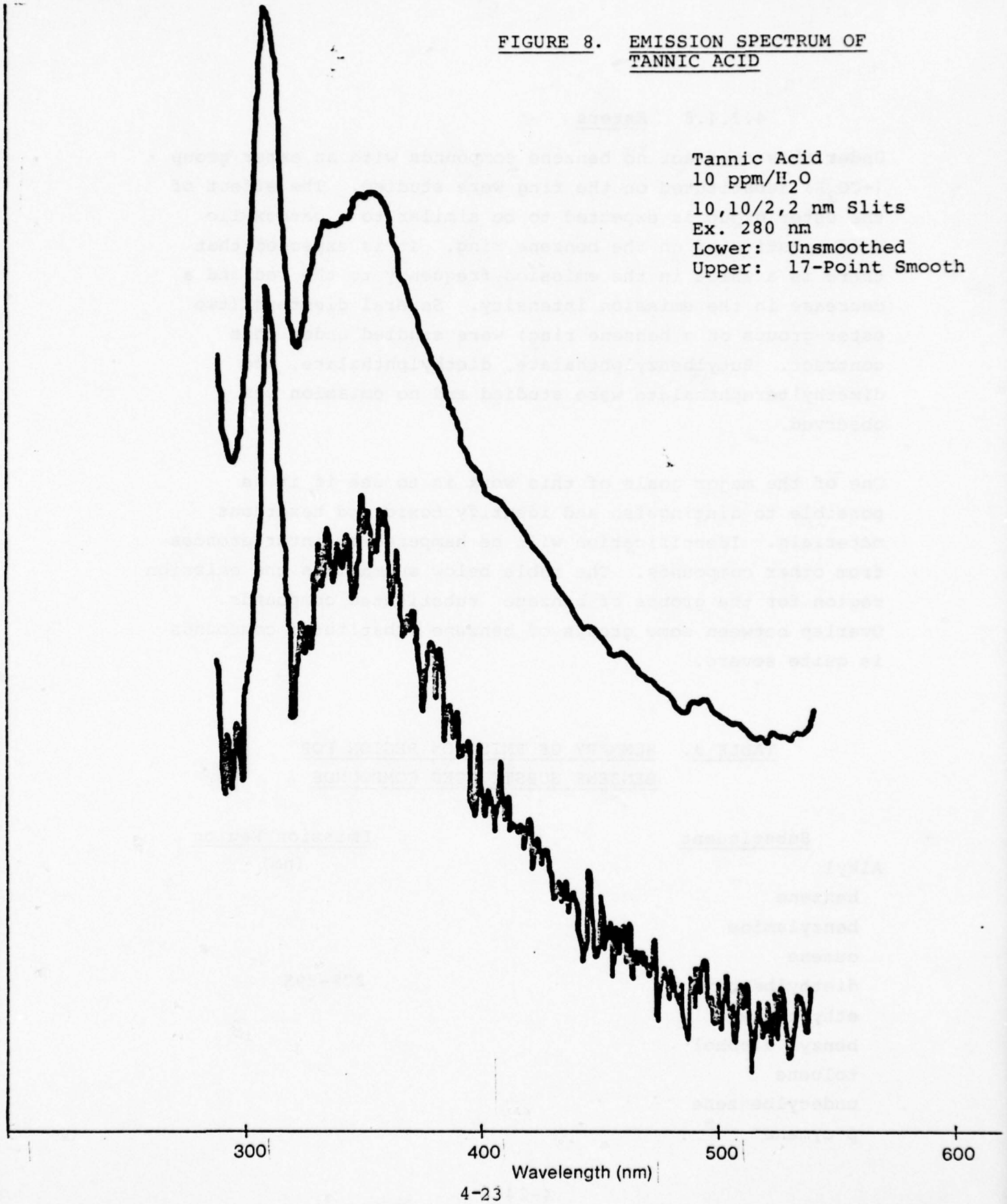
Salicyclic acid has a detection limit similar to phenol indicating that the carboxylic acid may not have a large diminishing effect on the emission intensity in the case. Gallic acid which is the carboxylic acid derivative of pyrogallol shows the wavelength shift associated with the acid group. The emission maximum of pyrogallol occurs at 335 nm while the emission maximum of gallic acid occurs at 346 nm. The fluorescence of tannic acid in water is weak and as a result very noisy. It is possible to apply a smoothing routine to this data to get better results. The smoothing algorithm is based upon a moving least-squares fit to a small number of data points. A quadratic cubic smoothing polynomial with a minimum of five points is used. The number of points in the smoothing function is an odd integer value to preserve symmetry about the central point, and is normally much smaller than the total number of points. Edwards and Wilson (38) in a study of noise-free gaussian lines, concluded that the smoothing range (number of data points times the data internal) should be ≤ 0.7 the full width at half maximum (FWHM) for a peak distortion of <10%. Enke and Meman(39) conclude that for a single pass smooth, the maximum signal to noise improvement is obtained by a smoothing range equal to approximately twice the FWHM. Generally band distortion was avoided at the expense of poorer signal to noise. In most cases the number of points which spans the FWHM of the narrowest band present was chosen. If the narrowest band is a Raman band

or other less interesting feature, the smoothing range might be enlarged to match that of the analyte (i.e. the tannic acid spectrum, Figure 8). Figure 8 shows both the unsmoothed and smoothed fluorescence curve for tannic acid.

The ($-SO_3H$) group has no effect on the emission frequency or emission intensity. This effect can be seen in the data for toluene and p-toluene sulfonic acid. The emission maxima for these compounds occur at the same point within experimental error and the detection limits for both of these compounds is similar.

Anisoyl chloride and benzoylchloride showed no fluorescence emission. This result is not surprising due to the presence of the acid and halogen substituents on the benzene ring.

FIGURE 8. EMISSION SPECTRUM OF TANNIC ACID



4.2.4.8 Esters

Under this contract no benzene compounds with an ester group ($-CO_2R$) substituted on the ring were studied. The effect of the ester group is expected to be similar to a carboxylic acid substituted on the benzene ring. It is expected that there is a shift in the emission frequency to the red and a decrease in the emission intensity. Several diesters (two ester-groups on a benzene ring) were studied under this contract. Butylbenzylphthalate, diethylphthalate, and dimethylterephthalate were studied and no emission was observed.

One of the major goals of this work is to see if it is possible to distinguish and identify toxic and hazardous materials. Identification will be hampered by interferences from other compounds. The table below summarizes the emission region for the groups of benzene substituted compounds. Overlap between some groups of benzene substituted compounds is quite severe.

TABLE 9. SUMMARY OF EMISSION REGION FOR BENZENE SUBSTITUTED COMPOUNDS

Substituent	Emission Region (nm)
Alkyl	
benzene	
benzylamine	
cumene	
diethylbenzene	279-295
ethylbenzene	
benzyl alcohol	
toluene	
undecylbenzene	
p-cymene	

TABLE 9. SUMMARY OF EMISSION REGION FOR BENZENE SUBSTITUTED COMPOUNDS (con't.)

Substituent	Emission Region (nm)
(Alkyl con't.)	
dodecylbenzene	
o-xylene	
triethylbenzene	279-295
m-xylene	
Hydroxy	
mono-hydroxy	
phenol	
nonylphenol	
o-cresol	
p-cresol	
o-tert-butylphenol	288-300
p-tert butylphenol	
2,4-dimethylphenol	
3,5-dimethylphenol	
dihydroxy	
hydroquinone	
resorcinol	303-326
catechol	
trihydroxy	
pyrogallol	395
Cyano	
benzonitrile	287

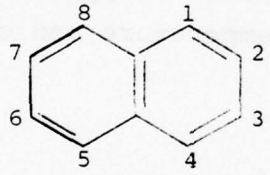
TABLE 9. SUMMARY OF EMISSION REGION FOR BENZENE SUBSTITUTED COMPOUNDS (con't.)

Substituent	Emission Region (nm)
Amino	
aniline	
methylaniline	
p-toluidine	316-328
4-chloro-o-toluidine	
p-chloroaniline	
Halo	
p-chlorotoluene	288-305
p-chlorophenol	
Acid	
phthalic	
gallic	340-409
salicylic	

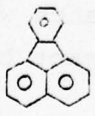
4.2.5 Polynuclear Aromatic Hydrocarbons (PAH)

In general, PAH have high quantum efficiencies of fluorescence allowing detection at low levels and tend to have sharp vibronic structure even at room temperature. The sharp vibronic structure and high quantum efficiency can be seen in compounds like benzo(a)pyrene, benzanthracene and dibenzanthracene. The fusing together of benzene rings in a sequence such as benzene, naphthalene, and anthracene, results in a decrease in energy between the lowest excited singlet and ground states. This results in a progressive movement of the fluorescence from the ultraviolet to the visible with anthracene emitting in the blue.

The emission maxima for benzene, naphthalene and anthracene show the expected shift: 279 nm, 323 nm, and 378 nm, respectively. Within this same series of linear polynuclear aromatic hydrocarbons the fluorescence yield increases as evidenced by the change in detection limit. There is greater than a 1000 fold change in quantum yield from benzene to anthracene. In most cases there is no significant wavelength shift for linear polynuclear aromatic hydrocarbons when the solvent is changed from a non-polar solvent like cyclohexane to a polar one like ethanol. The lack of solvent effect can be seen in the results for anthracene (section 3) where data was taken in both cyclohexane and ethanol. Alkyl substitution on a polynuclear aromatic hydrocarbon causes a red shift in the fluorescence spectrum. In large systems like naphthalene and anthracene this shift is dependent upon the positions of the substituent groups and are usually additive. Substituents placed in 2,3,6 and 7 positions of naphthalene have a larger effect on shifting spectra to



longer wavelengths than substituents in the 1,4,5, and 8 positions (5). Anthracene which can be considered a 2,3, or 6,7 substituted napthalene causes a 50 nm shift in emission maxima.

Acenaphthalene,  which can be considered an alkylbridged naphthalene has little effect on the emission maxima of naphthalene. Fluoranthene,  which can be considered a substituted naphthalene (35) causes a large shift in emission maxima primarily due to the effect of the benzene ring. The amino group in 1-naphthylamine produces a large (50 nm) red

shift, a loss in structure and a 20-fold decrease in detection limit. Heavy atom substitution as in chloronaphthalene produces no significant wavelength shift but does cause a reduction in the fluorescence efficiency. This can be seen in the five-fold poorer detection limit for chloronaphthalene. Tetrahydronaphthalene is structurally more like an alkyl substituted benzene. Its emission maximum is only slightly shifted from benzene and its width at half maximum is similar. There is a slight improvement in detection limit for tetrahydronaphthalene when compared to benzene similar to other alkyl substituted benzenes.

The other PAH studied in this contract can be considered bent systems. Naphthalene and anthracene are linear systems whereas benzanthracene, chrysene, 1,2,5,6-dibenzanthracene and benzo(a)-pyrene are bent systems. Anthracene, benzanthracene, chrysene, 1,2,5,6-dibenzanthracene and benzo(a)pyrene exhibit sharp vibronic structure at room temperature and can be detected at 1-10 ppb levels.

4.2.6 Heteroatom Compounds

The presence of a heteroatom greatly affects the luminescence of aromatic compounds. Heteroatoms possess lone pairs of nonbonding electrons which can undergo photochemical changes and compete with luminescence. Heterocyclic compounds (heteroatom incorporated in a ring) are usually very basic and the fluorescence and phosphorescence will be dependent on the choice of solvent. Under this contract both heterocyclic and heteroatom compounds were studied.

In several samples the heteroatom separated two benzene rings. These samples included diphenylether, diphenylamine, diphenyldichlorosilane and diphenylhydrazine. The results for these samples are varied. Diphenyldichlorosilane is much like benzene.

There is little change in the emission maximum and the detection limit is similar to benzene. In the case of diphenylether and diphenylamine there is a slight red shift from benzene, 13 and 45 nm respectively, with a small improvement in the detection limit for diphenylether. Diphenylamine underwent photochemical changes as the spectrum was being run. Diphenylhydrazine exhibited no fluorescence which may be related to the instability of the compound to oxidation.

Piperazine, acridine and quinoline were the heterocyclic compounds studied under this contract. Piperazine was non fluorescent. This result is not unexpected for saturated heterocyclic systems. Both acridine and quinoline were fluorescent. The fluorescence bands of acridine in neutral solution are located in the same spectral region as anthracene. The spectrum of acridine at room temperature is more diffuse but the structure becomes resolved at low temperature. The fluorescence emission of acridine is complicated by the presence of impurities and may be undergoing photochemical changes. The acridine emission is stronger in ethanol than in cyclohexane which is consistent with the increase in polarity of the solvent (36). Quinoline in non-polar solvents has an $n-\pi^*$ lowest excited state and is virtually non-fluorescent. In polar solvents the position of the $\pi-\pi^*$ and $n-\pi^*$ state reverses and gives rise to fluorescence emission. Quinoline was studied in cyclohexane, a non-polar solvent, and ethanol. The true emission is complicated by the presence of an impurity making identification of quinoline fluorescence difficult.

4.2.7 Oils

It is not surprising that the oils studied under this contract, (castor, coconut, cod liver, lard, linseed, olive, palm, peanut and soya bean) were for the most part weakly

fluorescent. The major constituents of these oils are saturated and unsaturated fatty acids which are not likely to fluoresce. Most of the oils had to be studied at fairly high concentrations (200-400 ppm) in order to see any fluorescence at all. This weak fluorescence is probably due to certain proteins or other natural products which are fluorescent and present in these oils. Since oils are complex mixtures it was important to excite at several different wavelengths. In several cases, two different emissions were obtained.

The results for the oils studied are tabulated below.

TABLE 10. OILS STUDIED UNDER CONTRACT

Oil	Conc. (ppm)	Solvent	λex (nm)	λem (nm)	O.D.	Comment
Castor Oil	390	ethanol	290	328	.025	Relatively strong single emission.
	286	cyclohexane	280	---	.051	Weak emission shoulder on solvent Raman.
	286	cyclohexane	320		>.01	Weak emission at 420 nm.
Coconut Oil	286	cyclohexane	290	330	>.01	Weak fluorescence occurs at both 280 and 290 nm excitation wavelengths, no emission occurs at 350 nm excitation.
Cod Liver Oil	323	cyclohexane	260	320	.027	Excitation at 260 nm and 280 nm produce similar emission spectra. Excitation at 350 nm produces a long wavelength emission centered at 500 nm.
	323	cyclohexane	280	320	.029	
	323	cyclohexane	350	500	.021	

TABLE 10. OILS STUDIED UNDER CONTRACT (con't.)

Oil	Conc. (ppm)	Solvent	λex (nm)	λem (nm)	O.D.	Comment
Cottonseed Oil	305	cyclohexane	280	320	.119	Excitation at 280 nm and 320 nm produced weak and different emissions for both wavelengths.
	305	cyclohexane	320	380	>.01	
Lard	287	cyclohexane	270	330	.045	Only a very weak emission was seen when the sample was excited at 270 nm. Long wavelength excitation did not produce any long wavelength emission.
Linseed Oil	355	cyclohexane	300	418	.036	Shows relatively strong emission when excited at 300 nm.
Olive Oil	237	cyclohexane	260	320	.076	Shows very weak emission at both excitation wavelengths.
	290	cyclohexane	310	---	.01	
Palm Oil	300	cyclohexane	260	320	.012	Shows two different and relatively weak emissions when excited at 260 and 350 nm.
	310	cyclohexane	350	500	>.01	
Peanut Oil	249	cyclohexane	260	320	.038	Very weakly emitting oil, almost no detectable emission.
	249	cyclohexane	290	320	.011	
Soya bean Oil	290	cyclohexane	270	---	.037	Very weakly emitting oil; almost no detectable emission.
	290	cyclohexane	320	---	.01	

4.2.8 Herbicides and Insecticides

Fluorescence has been used for the identification and quantitation of herbicides and insecticides. Solution methods have been developed and can be very sensitive in certain cases but care must be taken that impurities do not interfere with the measurement. In general, fluorescence analysis of herbicides and insecticides usually involves preparation on thin layer chromatography (TLC) (37). Thin layer chromatography relies on four methods for analysis. These include 1) the native fluorescence of the compound, 2) fluorogenic labelling, 3) release of a fluorescent chelating agent through complexation with the herbicide or insecticide or 4) conversion of a non-fluorescent compound to a fluorescent compound by means other than addition of a labelling agent. The TLC method incorporates several errors such as reproducibility of spot size, uniformity of the spot and weighing and integration to quantitate the amount of herbicide or insecticide present. Direct analysis would be the best way to analyze these materials. Several herbicides and insecticides studied under this contract can be measured directly. The results of our findings are tabulated below. (See Table 11.)

TABLE 11. SUMMARY OF HERBICIDES AND INSECTICIDES STUDIED

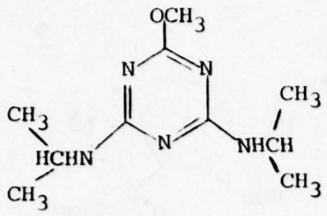
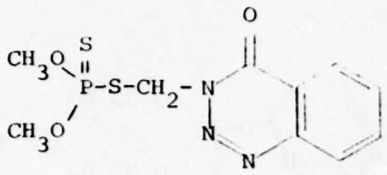
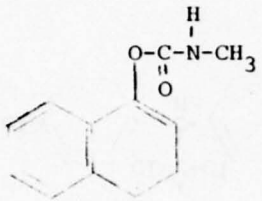
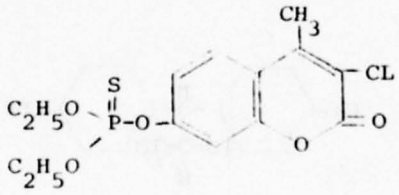
COMPOUND	TYPE	STRUCTURE	λ ex (nm)	λ em (nm)	DETECTION LIMIT (PPM)	COMMENT
Atrazine	herbicide		290	350	300	Very weakly fluorescent.
Azinphosmethyl	insecticide		340	420	4	More strongly fluorescent in ethanol than cyclohexane.
Carbaryl	insecticide		285	335	.01	-----
Coumaphos	insecticide		320	377	0.3	-----

TABLE 11. SUMMARY OF HERBICIDES AND INSECTICIDES STUDIED (Con't.)

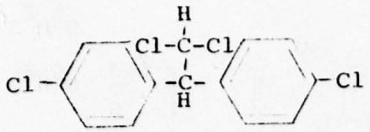
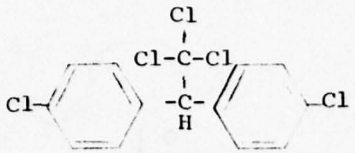
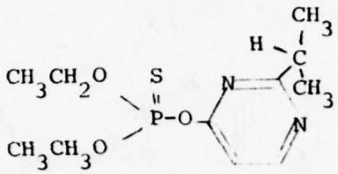
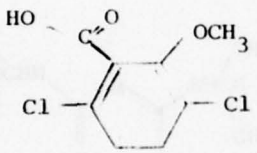
COMPOUND	TYPE	STRUCTURE	λex(nm)	λem(nm)	DETECTION LIMIT (PPM)	COMMENT
DDD	insecticide		240	294	4	
DDT	insecticide		245	291	7	Separation of DDD and DDT by fluorescence would be difficult.
Diazinon	insecticide		---	---	---	
Dicamba	herbicide		310	420	0.9	

TABLE 11. SUMMARY OF HERBICIDES AND INSECTICIDES STUDIED (Con't.)

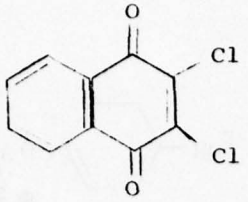
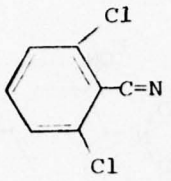
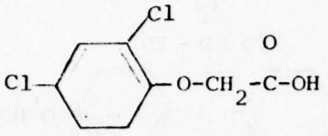
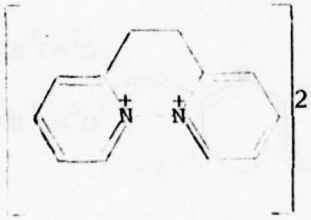
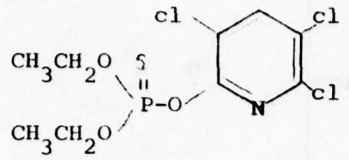
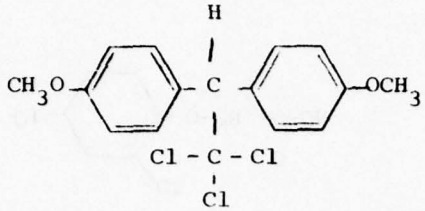
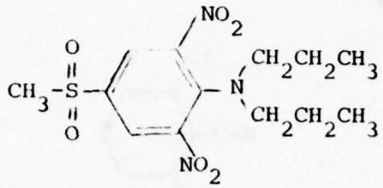
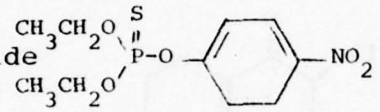
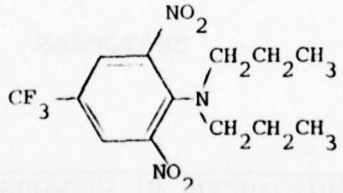
COMPOUND	TYPE	STRUCTURE	λ ex(nm)	λ em(nm)	DETECTION LIMIT (PPM)	COMMENT
Dichlone	herbicide		---	---	---	Non-emitter at room temperature, exhibits phosphorescence at 77°K.
Dichlorobenil	herbicide		285	312	0.6	
2,4,-D 2,4-Dichlorophenoxyacetic acid	herbicide		270	310	30	
Diquat dibromide	herbicide		310	348	.05	

TABLE 11. SUMMARY OF HERBICIDES AND INSECTICIDES STUDIED (CON'T)

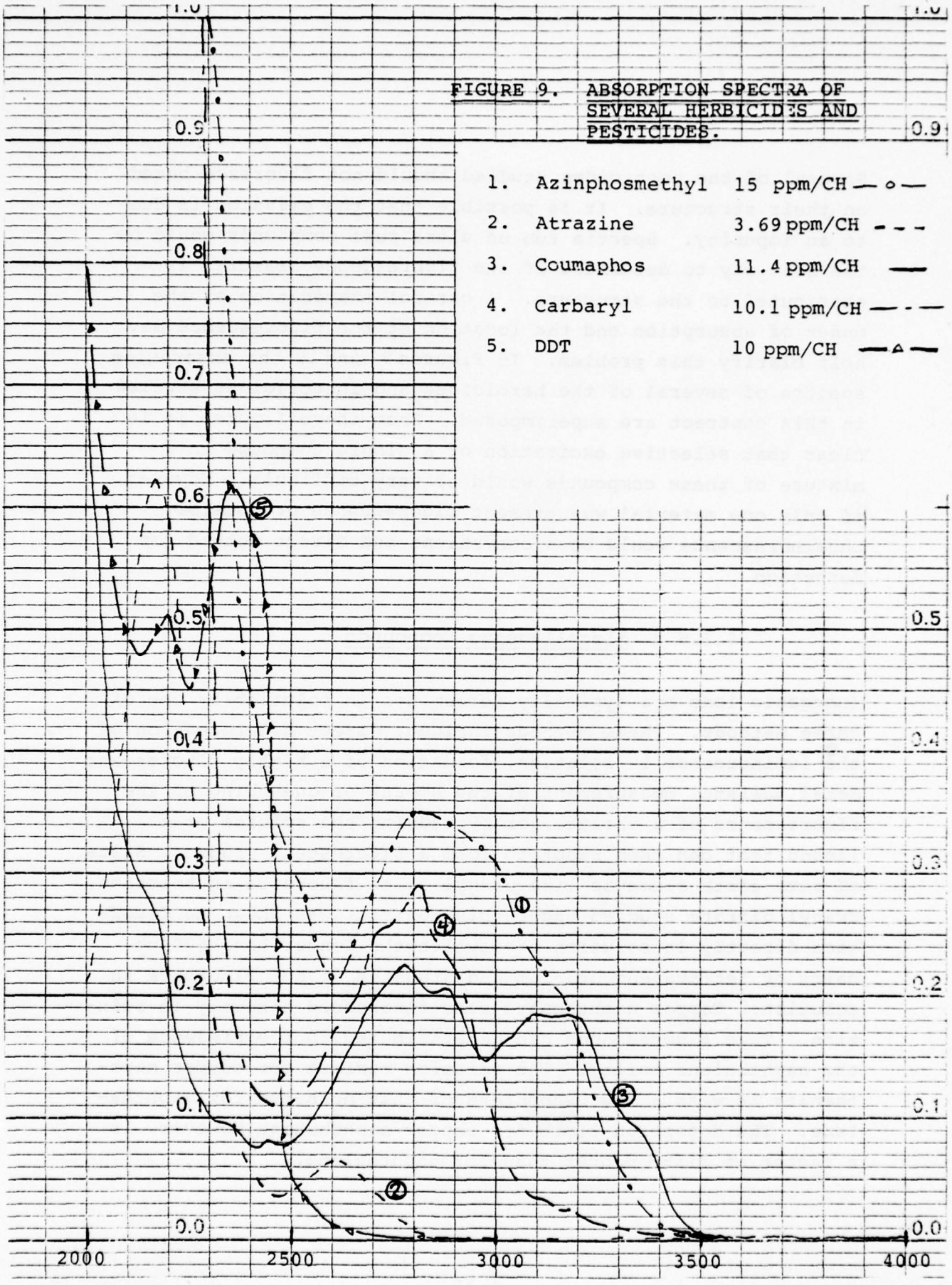
COMPOUND	TYPE	STRUCTURE	λ ex (nm)	λ em (nm)	DETECTION LIMIT (PPM)	COMMENT
Durban (Chloropyrifos)	insecticide		280	326	0.5	
Methoxychlor	insecticide		270	299	0.8	
Nitralin	herbicide		---	---	---	Not run-presence of nitro groups strongly quenches fluorescence.
Parathion	insecticide		---	---	---	
Trifluralin	herbicide		---	---	---	Not run-presence of nitro groups strongly quenches fluorescence.

Several of the pesticides studied should not fluoresce based on their structure. It is possible that the emission is due to an impurity. Spectra run on ultra pure compounds would be the best way to determine if the fluorescence measured is attributed to the structure. A careful examination of the onset of absorption and the location of the fluorescence may help clarify this problem. In Figures 9 and 10 the absorption spectra of several of the herbicides and insecticides studied in this contract are superimposed. From these figures it is clear that selective excitation of a single compound in a mixture of these compounds would be very difficult. However, if only one material was present fluorescence or possibly phosphorescence would be a convenient and direct method for detection.

4.2.9 Miscellaneous Compounds

Inorganic ions are typically determined in solution by one of three methods. These methods include, direct determination of the luminescence in solution, formation of a highly fluorescent metal chelate, measurement of the amount of quenching of the fluorescence of a chelate, or by causing the release of a ligand that can then react to form a fluorescent product. Salts of rare earth elements like uranyl salts fluoresce in solution. Uranyl nitrate studied under this contract was shown to fluoresce directly in solution at wavelengths longer than 500 nm. Salts of tetravalent uranium and uranates do not fluoresce in solution. Copper naphthenate also fluoresced directly in solution. This fluorescence can be attributed to the presence of the naphthalene moiety. The emission maximum for copper naphthenate is with a few nanometers of that measured for naphthalene. The detection limit for copper naphthenate however, is a factor of fifty poorer than for naphthalene.

FIGURE 9. ABSORPTION SPECTRA OF SEVERAL HERBICIDES AND PESTICIDES.



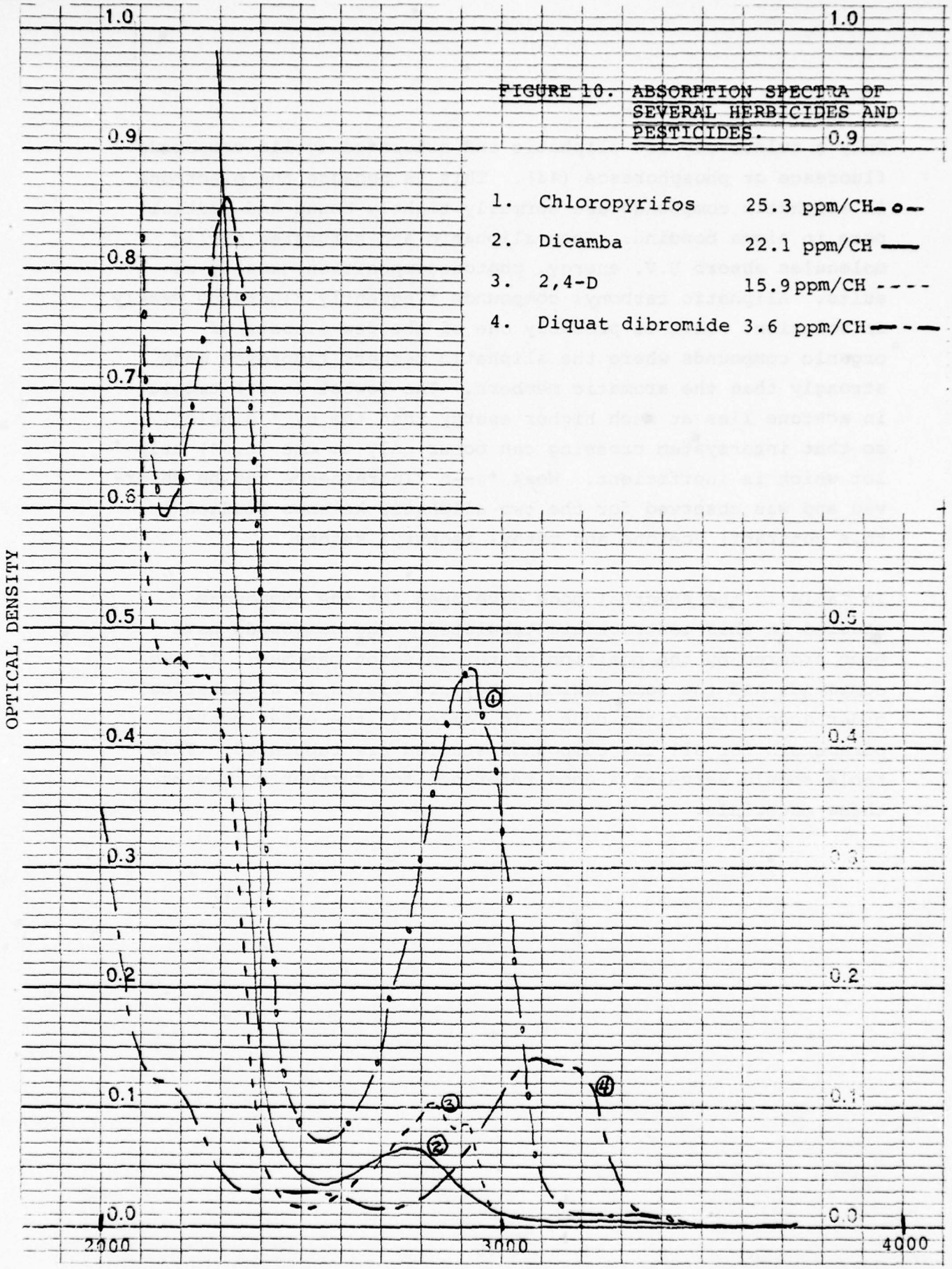


FIGURE 10. ABSORPTION SPECTRA OF SEVERAL HERBICIDES AND PESTICIDES.

Only a relatively few aliphatic and saturated cyclic compounds fluoresce or phosphoresce (43). This is because the electrons in aliphatic compounds are normally tightly bound and participate in sigma bonding. When aliphatic and saturated cyclic molecules absorb U.V. energy, photodecomposition usually results. Aliphatic carbonyl compounds frequently fluoresce weakly in solution. This is probably one of the few classes of organic compounds where the aliphatic members fluoresce more strongly than the aromatic members. The lowest (π,π^*) triplet in acetone lies at much higher energy than the n,π^* singlet, so that intersystem crossing can occur only to the (n,π^*) triplet which is inefficient. Weak $^*\pi$—n fluorescence can be observed and was observed for the two aliphatic ketones studied in this contract; acetone and methyl isobutyl ketone.

In Table 12 the spectral code developed for the compounds studied in this contract are tabulated. The compounds have been ordered by the position of the emission maximum. If two compounds had the same maxima, they are listed in alphabetical order according to the code. In Table 13, the experimental parameters for all the compounds studied are tabulated. This table should serve as a good reference for further work with these materials.

TABLE 12. LIST OF CODED SPECTRA

Spectral Code	Compound
279-24-3(2)-BNZ	Benzene
280-28-1(3)-BMA	Benzyltriethylammonium Cloride
283-27-1(2)-BZA	Benzylamine
283-28-2(1)-CUM	Cumene
283-28-1(2)-DEB	Diethylbenzene
283-26-2(2)-ETB	Ethylbenzene
283-34-1(2)-TPT	Turpentine
284-27-2(1)-BAL	Benzyl alcohol
284-27-2(2)-THN	Tetrahydronaphthalene
284-27-2(2)-TOL	Toluene
284-32-2(3)-UDB	Undecylbenzene
285-28-1(2)-CMP	p-Cymene
285-30-2(2)-DDS	Dichlorodiphenylsilane
285-30-3-DDB	Dodecylbenzene
285-28-1(1)-TAP	p-Toluene sulfonic acid
285-30-1-XLO	o-Xylene
287-28-2(1)-BZN	Benzonitrile
288-29-1(3)-CTN	p-Chlorotoluene
288-30-1(2)-PHN	Phenol
288-62-1(1)-TCP	Tricresyl phosphate
291-26-1(2)-DPE	Diphenylether
291-28-1(1)-DDT	DDT
292-28-1(2)-TEB	1,3,5-Triethylbenzene
293-30-1-CRO	o-Cresol
294-30-1(2)-DDD	DDD
295-30-1(1)-BOP	o-tert-Butylphenol
295-31-1(1)-BTP	p-tert-Butylphenol
295-28-1(1)-DPM	3,5-Dimethylphenol
295-28-1-XLM	m-Xylene
297-30-1(1)-PEN	Polyethoxylated nonylphenol
298-28-1-NNP	Nonylphenol
299-30-1(2)-CRP	p-Cresol
299-30-1(1)-MTC	Methoxychlor
300-31-1-DMH	2,4-Dimethylphenol

TABLE 12. LIST OF CODED SPECTRA (con't.)

Spectral Code	Compound
303-39-1(1)-RSC	Resorcinol
304-30-1(1)-BPA	Bisphenol A
305-30-1-CPN	p-Chlorophenol
305-30-2(2)-DOW	Dowtherm
306-32-2(2)-STY	Styrene
307-48-1-DEP	Diethylphthalate
307-35-1(2)-MSR	∝-Methylstyrene
310-46-1-CTC	Catechol
310-46-1(1)-DCA	2,4-Dichlorophenoxyacetic acid
310-N-2-DEG	Diethylene glycol
310-64-1-WCA	Carnauba Wax
312-30-1(2)-DIB	Dichlorobenil
316-32-1-ANC	Aniline
317-35-1(1)-PC4	Aroclor 1242
317-35-2(1)-PC5	Aroclor 1254
320-N-1-DEP	Diethylphthalate (Ex. 280nm)
320-N-1-OCL	Cod Liver Oil (Ex. 260nm)
320-N-1-OCL	Cod Liver Oil (Ex. 280nm)
320-N-1(1)-OCS	Cottonseed Oil (Ex. 280nm)
320-N-1-OOL	Olive Oil
320-60-1-OPM	Palm Oil (Ex. 260 nm)
320-N-1-OPN	Peanut Oil
323-20-4(3)-ACN	Acenaphthene
323-24-2(3)-NPT	Naphthalene
325-35-1-MAN	n-Methylaniline
325-34-1(1)-TLI	p-Toluidine
326-60-1(2)-CNN	Copper naphthenate
326-52-1-DUR	Chloropyrifos (Dursban)
326-38-1(1)-HDQ	Hydroquinone
327-56-1-BRU	Brucine
328-38-1-CAP	p-Chloroaniline
328-34-3(4)-CNA	1-Chloronaphthalene
328-39-1(1)-COT	4-Chloro-o-toluidine
328-43-1-OCA	Castor Oil

TABLE 12. LIST OF CODED SPECTRA (con't.)

Spectral Code	Compound
330-N-1(1)-OCC	Coconut Oil
330-N-1-OLD	Lard
333-37-1(2)-DAM	Diphenylamine
335-36-2(3)-CBY	Carbaryl
335-86-1(1)-PGA	Pyrogallic acid
340-100-1-PHA	Phthalic acid
340-100-1-TNA	Tannic acid
346-77-1-GLA	Gallic acid
347-52-1(1)-SDB	Sodium dodecylbenzene sulfonate
348-41-1(1)-DOD	Diquat dibromide
369-32-2(3)-IND	Indene
377-74-1-COU	Coumaphos
377-55-1(1)-NAD	α-Naphthylamine
378-31-3(2)-ATH	Anthracene
380-N-1-OCS	Cottonseed oil (Ex. 320nm)
383-27-5(3)-CRY	Chrysene
386-28-4(1)-BAT	1,2-Benzanthracene
396-26-4(2)-DBA	1,2,5,6-Dibenzanthracene
400-N-1-MIK	Methyl isobutyl ketone
405-5-6(2)-BAP	Benzo(a)pyrene
409-64-1-SLA	Salicylic acid
410-N-1-ACT	Acetone
410-58-2-AZP	Azinphosmethyl/CH
418-105-1-OLS	Linseed Oil
420-52-2(1)-ACD	Acridine/ETOH
420-82-1-AZP	Azinphosmethyl/ETOH
420-70-1-DIC	Dicamba
430-94-2-ACD	Acridine/CH
464-91-2(3)-FLA	Fluoranthene
500-150-1-OCL	Cod Liver Oil (Ex. 330nm)
500-141-1-OPN	Palm Oil (Ex. 350nm)
520-56-3-UAN	Uranyl Nitrate

TABLE 13. SUMMARY OF EXPERIMENTAL PARAMETERS AND RESULTS.

	CODE	CONC (PPM)	SOL-VENT	λ_{exc} (nm)	λ_{max}^{em} (nm)	# PEAKS	WHM (nm)	# SHOULDER	DETEC-TION LIMIT (D.L.) (PPM)	λ_{DL} (nm)	COMMENTS
Acenaphthene	ACN	1.03	CH	290	323	4		3	.001	290	
Acetone	ACT	227	CH	290	410	1			212	290	
Acridine	ACR	96	CH	285/355	386/422	4/2		2/0			
	ACR	9.6	ETOH	290/355	357/415	2/2		1/1	.02/.04	290/355	
Aniline	ANL	15.5	CH	280	316	1			.037	280	
Anisoyl Chloride											No fluorescence data taken
Anthracene	ATH	1.03	CH	355	378	4		1	.001	355	
	ATH	1.55	ETOH	355	380	4		1	.001	355	
Aroclor 1242	PC4	131	CH	270	317	2	35	1	.3	270	
1254	PC5	129	CH	270	317	2	36	1	2	270	
Atrazine	ATZ	369	CH	290	~350	1	--		300	290	
Azinphosmethyl	AZP	112	CH	350	410	2	60		10	350	
	AZP	122	ETOH	340	420	2	80		4	340	
Benz(a)anthracene	BAT	1.1	CH	280	386	4		1	.003	280	
Benzene	BNZ	79	CH	250	279	3	24	1	2/4	250/265	
Benzonitrile	BZN	9.9	CH	260	287	2	28	1	.1/.1	260/270	
Benzo(a)pyrene	BAP	0.088	CH	370	405	6		2	.002	370	
Benzoyl chloride	BCL	104	CH	260							Non-fluorescent
Benzyl alcohol	BAL	99	CH	250	284	2	27	1	.1/.1	250/260	
Benzyl amine	BZM	118	CH	250	283	1	27	2	3/2	250/260	
Benzyl triethyl-ammonium chloride	BMA	210	H20	250	280	1	28		59	250	
Bisphenol A	BPA	10.5	ETOH	270	304	1	30	1	.04/.02	270/285	
Brucine	BRU	13.5	ETOH	280	327	1	56		2/2	280/295	
Butyl benzylphthalate	BBP										Non-fluorescent
O-tert-Butylphenol	BOP	21	CH	265	295	1	30	1	.1/.1	265/275	
p-tert-Butylphenol	BTP	17.5	CH	260	295	1	31	1	.6/.4	260/280	
Carbaryl	CBY	1.0	CH	285	335	2	36	2	.01	285	
Carnauba Wax	WCA	63.5	CH	260	310	1	64		42	260	
Castor Oil	OCA	390	ETOH	290	328	1	43	2	20	290	
	OCA	286	CH	280/320		1			180/300	280/320	
Catechol	CTC	8.7	H20	265	310	1	46		.4/.2	265/280	
4-Chloroaniline	CAP	17.2	CH	290	328	1	36	1	.2	290	
1-Chloronaphthalene	CNA	11.3	CH	290	328	3	34	4	.1	290	

TABLE 13. SUMMARY OF EXPERIMENTAL PARAMETERS AND RESULTS (con't.).

	CODE	CONC (PPM)	SOL-VENT	λ_{exc} (nm)	λ_{max}^{em} (nm)	# PEAKS	WHM (nm)	# SHOULDER	DETECTION LIMIT (DL) (PPM)	λ_{DL} (nm)	COMMENTS
p-Chlorophenol	CPN	101	CH	260	305	1	30		1/.1	260/285	
Chlorpyrifos (Dursban)	DUR	25.3	CH	280	326	1	52		1/.5	280/295	
p-Chlorotoluene	CTN	23.8	CH	265	288	1	29	3	1/.8	265/275	
p-Chloro-o-toluidine	COT	25	CH	290	328	1	39	1	.09	300	
Chrysene	CRY	1.0	CH	270	383	5			.002	270	
Coconut Oil	OCC	286	CH	290	330				100	290	
Cod Liver Oil	OCL	323	CH	300/280	420/320	1,1	-		260,140	260,280	
				340	500	1	150		65	330	
Copper Naphthenate	CNN	98	CH	260	326	1	60	3	3/1	260/280	
Cottonseed Oil	OCS	305	CH	280/320	320/380	-	-		165,300	280,320	
Coumaphos	COU	11.4	CH	320	377	1	74		.3	320	
o-Cresol	CRO	12.0	CH	265	293	1	30	1	.04	280	
p-Cresol	CRP	10.3	CH	265	299	1	30		.03	280	
Cumene	CUM	101	CH	250	283	2	28	1	3	250	
p-Cymene	CMP	11.8	CH	260	285	1	28	2	.4/.2	260/270	
DDD	DDD	61.	CH	240	294	1	30	2	4	240	
DDT	DDT	87	CH	245	291	2	28	2	7	245	
Diazinon	DZN										Non-fluorescent
1,2,5,6-Dibenzanthracene	DBA	.015	CH	300	396	4		2	.001	300	
Dicamba	DIC	22.2	H20	310	420	1	70		.9	310	
Dichlone	DCL	2.8	CH	280							Non-fluorescent
Dichlorobenil	DIB	108	CH	285	312	1	30		.6	285	
2,4-Dichlorophenoxy-acetic acid	DCA	159	CH	270	310	1	46	1	30	270	
Diethylbenzene	DEB	100	CH	255	283	1	28	2	.2/.1	255/270	
Diethylene glycol	DEG	202	CH	265	310	2	-	-	202	265	
Diethylphthalate	DEP	145/289	CH	260/280	300/320	1/1				280	
2,4-Dimethylphenol	DMH	10.5	CH	265	300	1	31	1	.2/.04	265/280	
3,5-Dimethylphenol	DPM	10.5	CH	265	295	1	28	1	.07/.03	265/280	
Dimethyl terephthalate	DMT										Non-fluorescent
2,4-Dinitroaniline	DNT										Non-fluorescent
4,6-Dinitro-o-cresol	DOC										Non-fluorescent
2,4-Dinitrophenol	DNP	10.4	H20	270	~350						Non-fluorescent
Diphenylamine	DAM	11.2	CH	290	333	1	37	2		290	Photochemical change
		1.2	CH	290	333	1	37	2		290	

TABLE 13. SUMMARY OF EXPERIMENTAL PARAMETERS AND RESULTS (con't.).

	CODE	CONC (PPM)	SOL-VENT	λ_{exc} (nm)	λ_{max}^{em} (nm)	# PEAKS	WHM (nm)	# SHOULDER	DETEC-TION LIMIT (D.L.) (PPM)	λ_{DL} (nm)	COMMENTS
Diphenyldichlorosilane	DDS	157	CH	260	285	2	30		3/2	260/270	
Diphenylhydrazine	DPH	32.6	ETOH								Non-fluorescent
Diquat dibromide	DQD	35.5	H20	310	348	1	41	1	.055	310	
Diuron	DIU										Not recieved
Dodecylbenzene	DDB	116	CH	250	285	3	30		*	250	Strong impurity
		116	CH	220	285	3	30		13.6	220	
Dowtherm A	DTH	10.8	CH	260	305	2	33	2	.035	260	
Ethylbenzene	ETB	103	CH	250	283	2	26		3.1/1.5	250/260	
Fluoranthene	FLA	1.0	CH	360	465	2	91	3	.005	360	
Gallic acid	GLA	103	H20	290	346	1	77		.70	290	
Hydroquinone	HDQ	1.1	H20	290	326	1	38	1	.025	290	
Indene	IND	175	CH	260	309	2	32	3	.12	260	
Lard	OLD	340	CH	270	330					270	
	OLD	287	CH	280	330	1				280	
Linseed Oil	OLS	355	CH	300	418	1	105		32.	300	
Methoxychlor	MOC	95	CH	270	299	1	30	1	1.3/0.8	270.280	
Methylaniline	MAN	10.8	CH	290	325	1	35		.01	290	
Methylene di-p-phenylene diisocyanate											No fluorescence data taken
Methyl isobutyl ketone	MIK	358	CH	290	400	1				290	
-Methyl styrene	MSR	105	CH	255	307	1	35	2	.12	255	
Naphthalene	NPT	10.5	CH	280	323	2	24	3	.02	280	
1-Naphthylamine	NAD	1.85	CH	325	377	1	55	1	.0012	325	
Nitraline											No fluorescence data taken
m-Nitroaniline	NTM										
Nonyl phenol	NNP	17.1	CH	265	298	1	28		.09	265	
Olive Oil	OOL	237	CH	260	~320	1				360	
	OOL	290	CH	310						310	
Palm Oil	OPM	300	CH	260	320	1	60		218	260	
			CH	350	500	1	140		300	350	
Parathion E	PTO	3.5	CH	280							Non-fluorescent
Peanut Oil	OPN	249	CH	260,290	320, 320	1					
Phenol	PHE	11.9	CH	265	288	1	30	2	.011/.007	265/275	
Phenyl ether	DPE	20.4	CH	265	291	1	36	1	.10	265	

TABLE 13. SUMMARY OF EXPERIMENTAL PARAMETERS AND RESULTS (con't.).

	CODE	CONC (PPM)	SOL-VENT	λ_{exc} (nm)	λ^{em}_{max} (nm)	# PEAKS	WHM (nm)	# SHOULDER	DETECTION LIMIT (D.L.) (PPM)	λ DL (nm)	COMMENTS
Phthalic acid	PHA	97	H20	280	330	1	100		84	280	
	PHA	228	H20	270	340	1	100		114	270	
Piperazine	PPZ	235	CH	280	~350	1					
Poly-ethoxylated nonyl-phenol	PEN	9.5	CH	265	297	1	30		.08,.03 17	265/280	
Pyrogallol	PGA	152	H20	270	335	1	86	1	30	270	
Quinoline	QNL	113	ETOH	275	321	5		2			
		113	ETOH	355	420	1	70	0			Photolyzes
		95	CH	275	336	3		2	.37	275	Photolyzes
		95	CH	350		2	57	1			Photolyzes
Resorcinol	RSC	10.1	H20	265	303	1	39	1	.135/05	265/280	
Salicylic acid	SLA	1.5	H20	300	409	1	64		.005	300	
Sodium dodecylbenzene-sulfonate	SDB	90	CH	290	347	1	52	2	.90	290	
Soya Bean Oil	OSB	290	CH	270,320					-,300	270,320	
Styrene	STY	1.1	CH	270	306	2	32	2	.03	270	
Tallow	TLO										No fluorescence data taken
Tannic acid	TNA	13	H20	280	340	1	100		.63	280	
1,2,3,4-Tetrahydro-naphthalene	THN	12.3	CH	260	284	1	27	2	.21/.13	260/270	
p-Toluidine	TLI	14.1	CH	290	325	1	34		.03	290	
Toluene	TOL	107	CH	250	284	2	27	1	2.1/1.6	250/215	
p-Toluene sulfonic acid	TAP	120	H20	260	285	1	28	1	2.1/1.5	260/265	
Tricresylphosphate	TCP	123	CH	260	288	1	66	1	.55/.35	260/270	
1,3,5-Triethylbenzene	TEB	122	CH	250	292	1	28	3	12.5/1.5	250/270	
Trifluralin	TFL										No fluorescent data taken
Turpentive	TPT	301	CH	260	283	1	34	3	31/13	260/270	
Undecylbenzene	UDB	87.3	CH	250	284	2	33	2	6.0	250	
Uranyl nitrate	UAN	61.	H20	290	520	3	56	2	6.1/10.5	290/330	
m-Xylene	XLM	114	CH	260	285	1	28	1	2.0/1.4	260/270	
o-Xylene	XLO	92	CH	260	295	1	30		1.5/1.3	260/270	
Zirconium acetate	ZCA										See text

5. SUMMARY AND CONCLUSIONS

The results obtained in this contract showed that fluorescence offers a useful analytical tool for identifying and quantifying toxic and hazardous materials. One hundred-nine compounds were studied and ninety-six compounds were determined to be fluorescent. Some compounds (i.e., non-petroleum oils) fluoresced very weakly. However, in many cases, the emission was strong and offered detection at reasonably low levels, <1 ppm.

Several compounds were studied in two solvents; cyclohexane and ethanol. For some compounds changing the solvent to a more polar one can lead to dramatic effects on peak location. This change can be explained in terms of the Franck-Condon principle. An electronic transition must occur while the photon is in the vicinity of the absorbing molecules in about 10^{-15} sec. This is 10^3-10^4 times faster than the rate of bond stretching so that an electronic transition occurs before any change in interatomic distance will occur. The molecule now in a Franck-Condon excited state readjusts to its new environment by a solvent reorientation in 10^{-12} sec and reaches an equilibrium excited state. Emission then occurs in 10^{-8} sec. Thus, in solution, the molecule enters into one excited state and leaves from another excited state of slightly different energy levels. This is why fluorescence and absorption spectra are subject to different solvent effects. For polar molecules the excited state is more polar than the ground state. Increasing the polarity of the solvent produces a greater stabilization of the excited rather than the ground state. Hence, a shift to longer wavelength is observed. This type of behavior is observed for almost all cases even when the solute and solvent are not polar because of the induced depole in the excited state. The magnitude of this shift is not great. Table 14 below summarizes the effect of solvent on anthracene absorption and fluorescence.

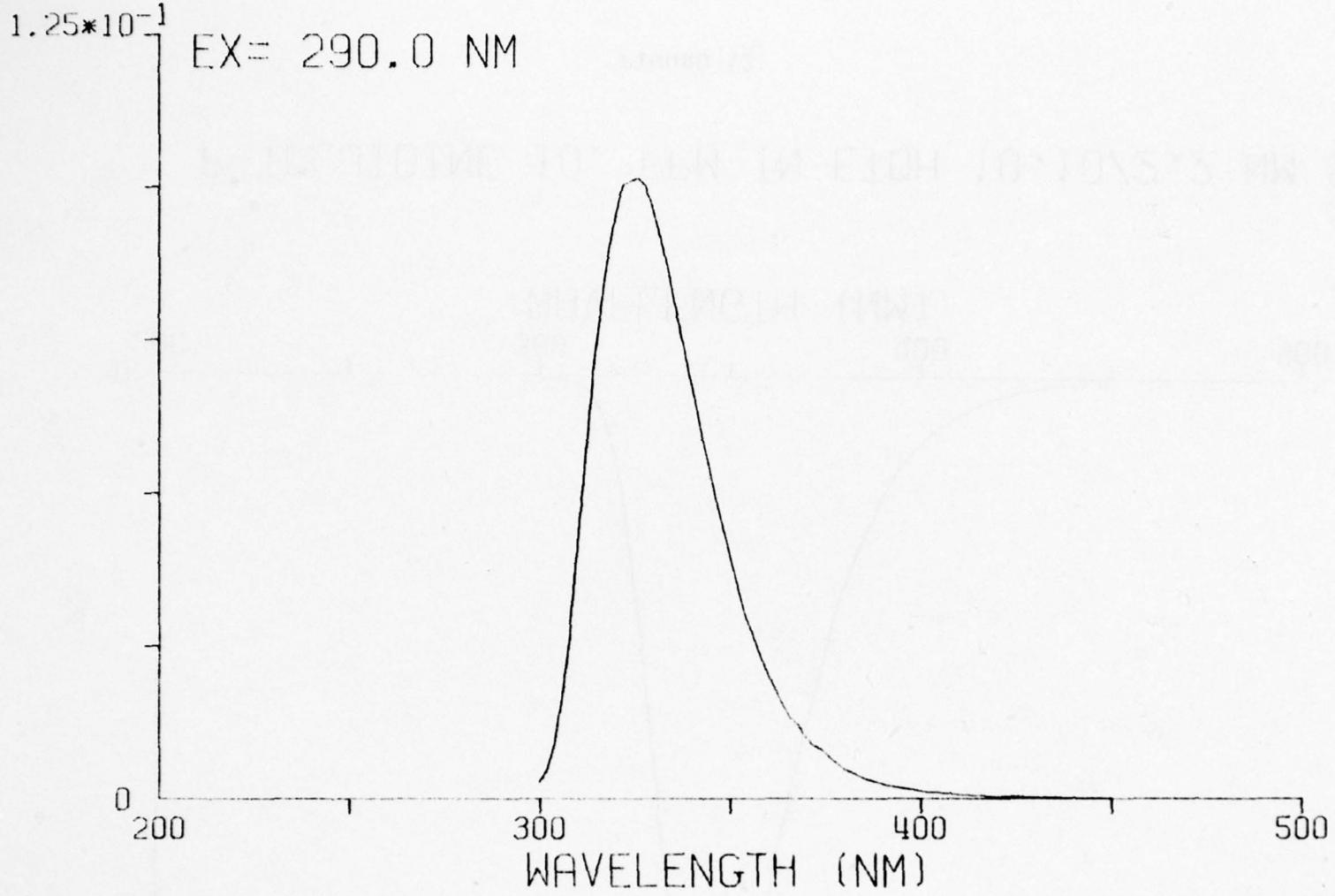
TABLE 14. EFFECT OF SOLVENT ON ANTHRACENE (45)

Solvent	ν_F cm^{-1}	λ_F nm
Vapor	27380	365
Hexane	26517	377
Methanol	26461	378
Dioxane	26220	381
Toluene	26170	382
Benzene	26116	383
Chlorobenzene	26064	384
Acetonitrile	25972	385
Formanide	25508	392
N-Methylformanide	25112	398

As further examples of this effect two other molecules were run in several solvents. Figure 11 shows the emission of p-toluidine in cyclohexane. The shift of the emission maximum to longer wavelength is clearly seen for p-toluidine in ethanol (Figure 12) and for a seventy percent solution of acetonitrile and water(Figure 13). A similar but not nearly as dramatic effect can be seen for p-tertbutylphenol in cyclohexane and ethanol (Figure 14 and 15). This solvent effect should be studied in great detail. It offers another parameter which may lead to further selectivity of the fluorescence method.

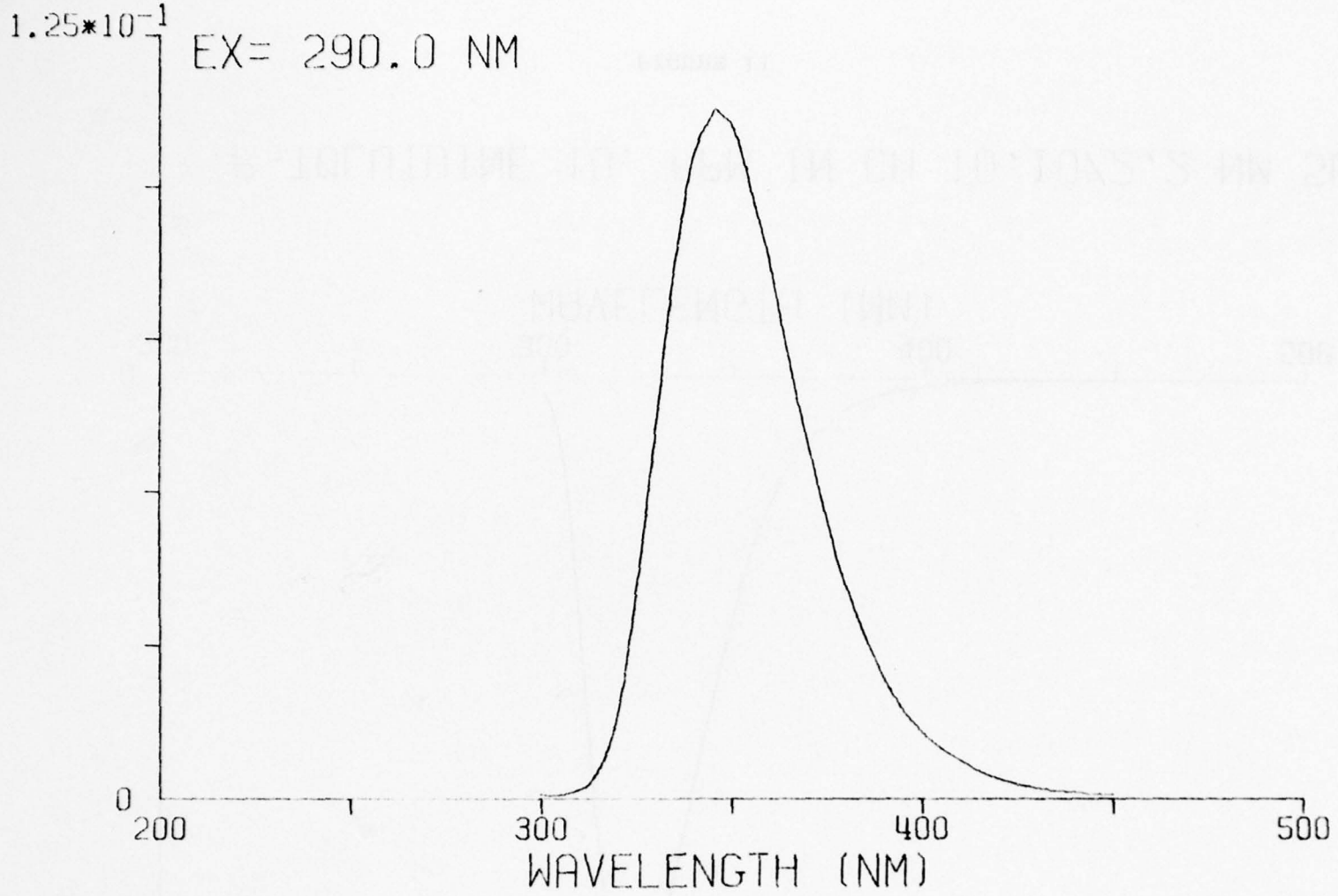
Impurities always present problems in analytical measurements. Several compounds studied under this contract showed fluorescing impurities. Attempts were made to separate the impurity emission from pure compound emission. This was not possible in all cases. Several compounds were determined to be fluorescent which based on their chemical structure should not be. This type of possible misassignment is due to the dominance of impurity emission. A careful examination of the absorption and fluorescence data may shed light on this problem.

1 /24/79



P-TOLUIDINE 10. PPM IN CH 10,10/2,2 NM SLITS

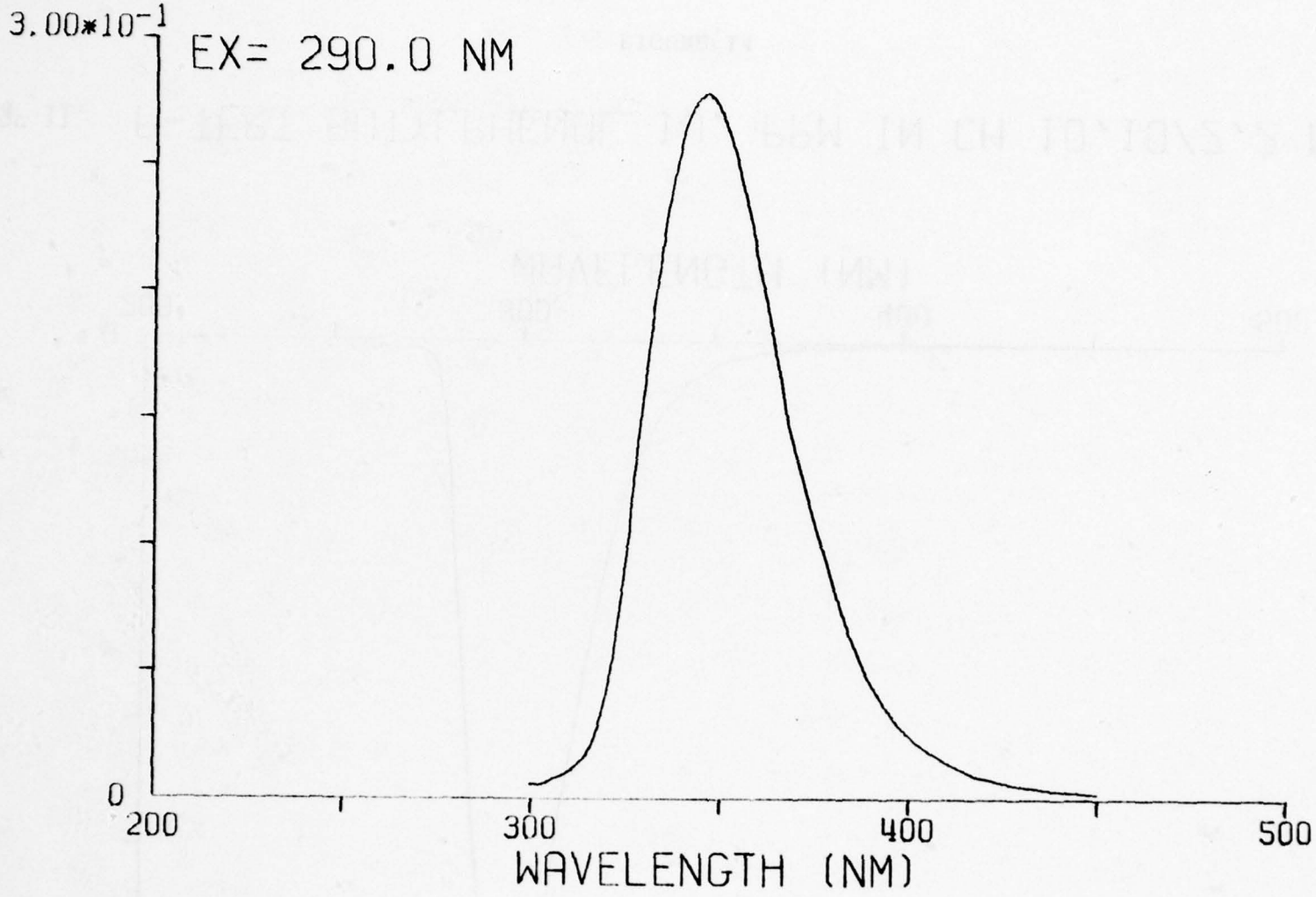
FIGURE 11



P-TOLUIDINE 10. PPM IN ETOH 10,10/2,2 NM SLITS

FIGURE 12

5 /9 /79



P-TOLUIDINE 10 PPM IN 70% CH3CN IN H20 10,10/2,2

FIGURE 13

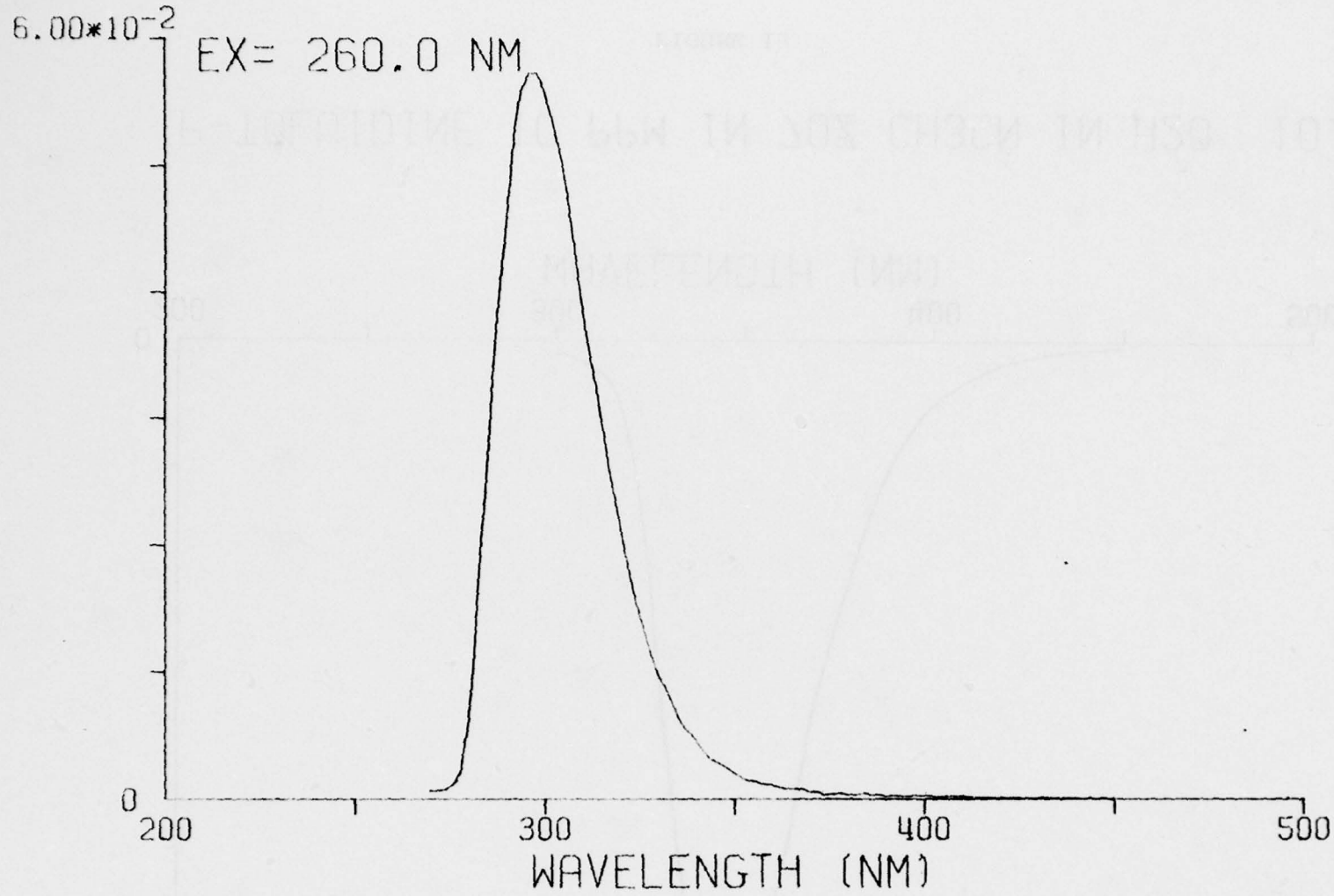
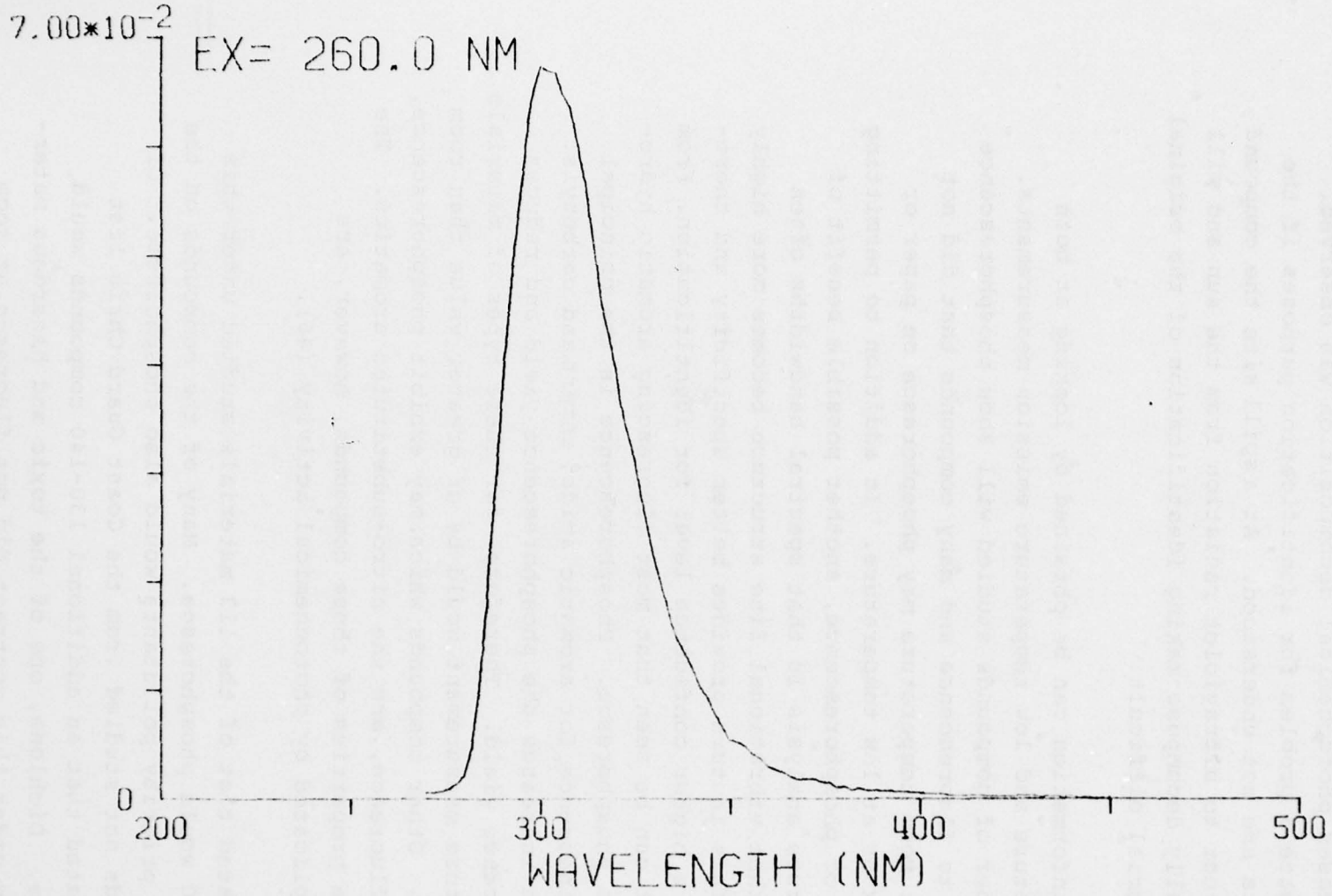


FIGURE 11. P-TERT BUTYLPHENOL 10. PPM IN CH 10,10/2,2 NM SLIT

FIGURE 14



FIGUPE 12. P-TERT BUTYLPHENØL 10. PPM IN ETØH 10,10/2,2 NM SL

FIGURE 15

In several cases photochemical decomposition was observed. This may create a problem for identification purposes if the photoproducts are not understood. At a spill site the compound will be subject to ultraviolet radiation from the sun and will photochemically decompose making identification of the original spilled material difficult.

Additional information can be obtained by looking at both room temperature and low temperature emission measurements. A large number of compounds studied will show phosphorescence in addition to fluorescence and many compounds that did not fluoresce at room temperature may phosphoresce on paper or other matrix or at low temperature. In addition to permitting observation of phosphorescence, another possible benefit of low temperature analysis is that spectral bandwidths often narrow, so that vibrational fine structure becomes more highly resolved. This in turn provides better specificity and therefore yields a higher confidence level for identification. From Table 15, it can be seen that most fluorescing aromatic hydrocarbons also phosphoresce. Phosphorescence is the principal form of luminescence for aromatic acids, esters and carbonyls. Halogenation increases the phosphorescence yield and reduces the fluorescence yield. Therefore, for these types of materials, low temperature measurement would be of greater value than room temperature. Other compounds which may exhibit phosphorescence, but rarely fluoresce, are the nitro-substituted aromatics. The luminescence properties of these compounds, however, are usually complicated by photochemical activity (46).

It is estimated that of the 113 materials studied under this contract 100 would phosphoresce. Many of the compounds on the EPA list of priority pollutants would also phosphoresce. Of the compounds not studied from the Coast Guard Chris list it is estimated that an additional 130-140 compounds would phosphoresce. Dichlone, one of the toxic and hazardous materials studied under this contract did not fluoresce at room temperature. However, it did phosphoresce quite strongly at

TABLE 15. EXPECTED INFLUENCE OF SUBSTITUENTS ON THE LUMINESCENCE OF AROMATIC HYDROCARBONS

Substituent	Effect On Fluorescence Wavelength(a)	Effect On Fluorescence Intensity(a)	Phosphorescence	Comments(b)
Alkyl	None	Slight Increase	Yes	For benzene derivatives, $\phi_F \cong \phi_P$ at L.T.
-OH,-OR	Increase	Increase	Yes	$\phi_P \geq \phi_F$ at L.T. Strong pH dependence of R.T. fluorescence
$-CO_2H, CO_2R$, -CO2NH	Increase	Large Decrease	Yes	$\phi_P >> \phi_F$ at L.T. Hydroxy and amino groups increase ϕ_F
O O -C-H,-C-R	Increase	Large Decrease	Yes	Behavior similar to acids, esters, etc.
$-NO, -NO_2$	---	Usually total quenching	Variable	ϕ_P Usually small $\phi_P > \phi_F$ in H-bonding solvents at L.T. (Often photochemically unstable)
-CN	None	Decrease	Yes	
-F,-Cl,-Br,-I	Increase	Increase	Yes	$\phi_P > \phi_F$ at L.T.
$-SO_3H$	None	None	?	

a. From Table 3-1 of Ref. 3

b. ϕ_F, ϕ_P represent fluorescence and phosphorescence quantum yields respectively

low temperature. The phosphorescence spectrum of Dichlone at two different excitation wavelengths are shown in Figures 16 and 17.

Further work in the above areas, along with quantum yield measurements, absorption and excitation spectra measurements, and analysis of photoproducts, will help establish luminescence techniques as a useful means for studying toxic and hazardous materials.

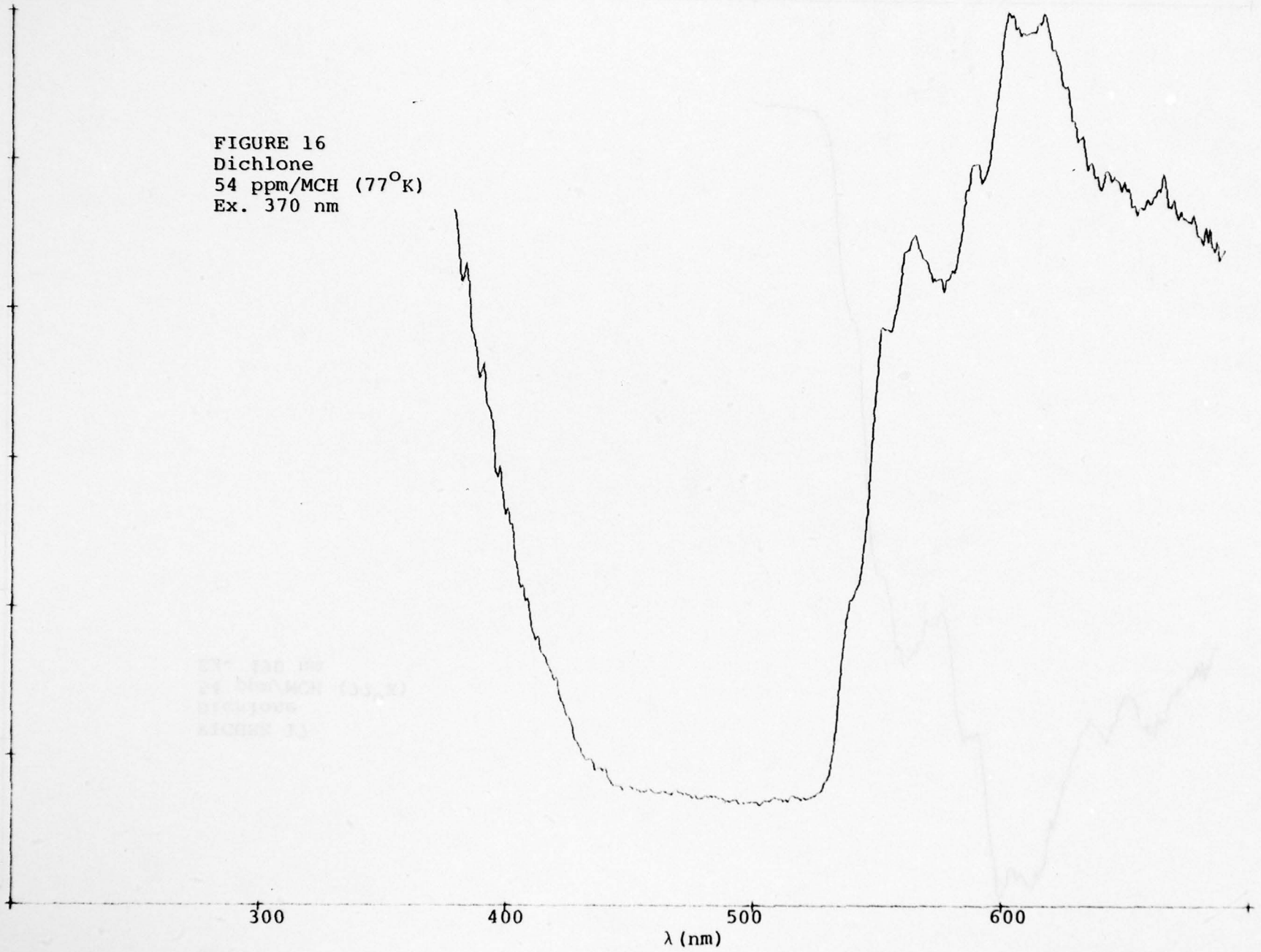
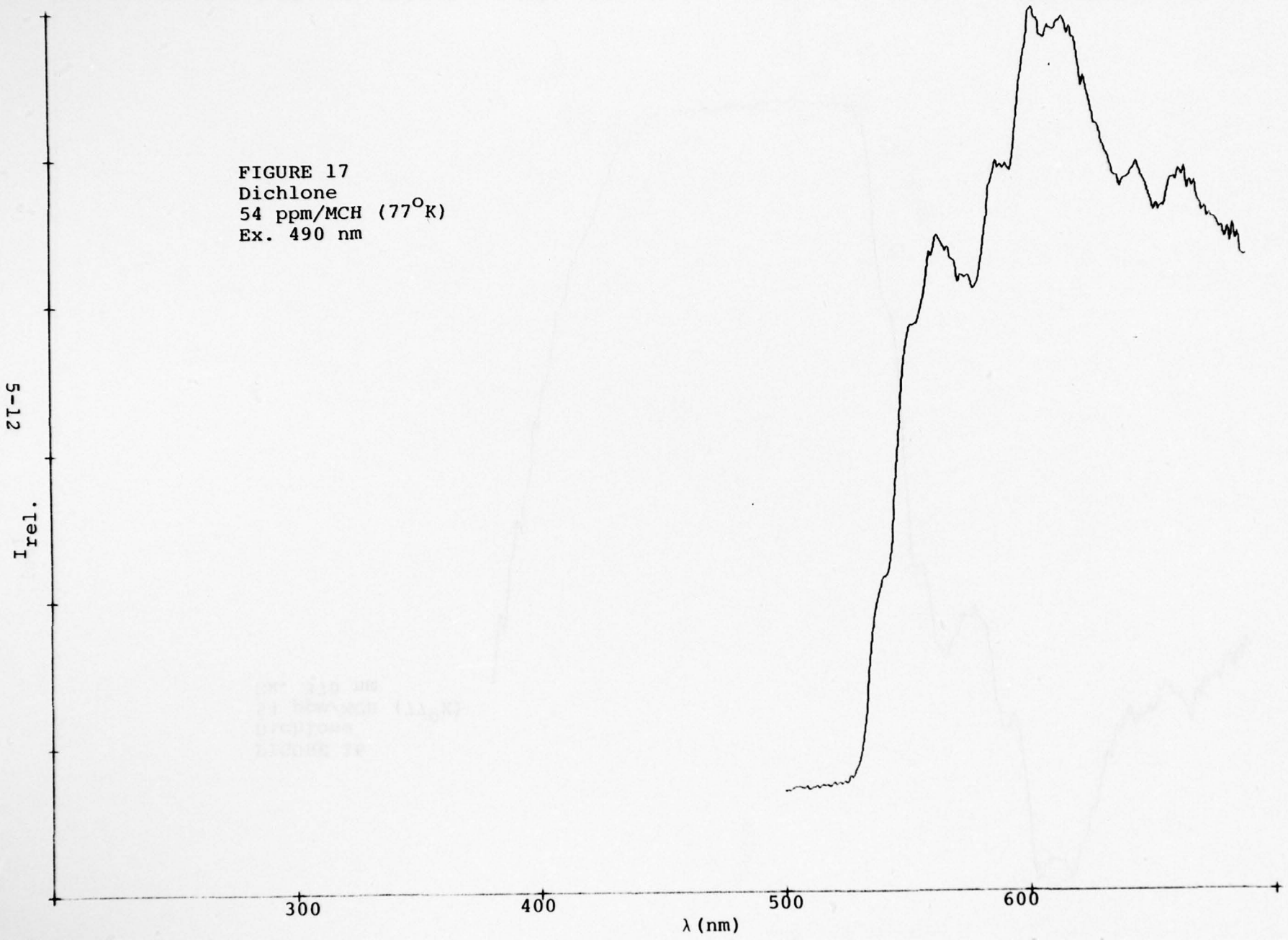


FIGURE 16
Dichlone
54 ppm/MCH (77°K)
Ex. 370 nm

FIGURE 17
Dichlone
54 ppm/MCH (77°K)
Ex. 490 nm



6. REFERENCES

1. S. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973.

2. R. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence", Wiley Interscience, New York, 1969.

3. D. M. Hercules, "Fluorescence and Phosphorescence Analysis" Interscience, New York, 1966.

4. P. Pringsheim, "Fluorescence and Phosphorescence" Interscience, New York, 1949.

5. I. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, 1971.

6. C. A. Parker, "Photoluminescence of Solutions", Elsevier, New York, 1968.

7. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1966.

8. J. Birks, "Photophysics of Aromatic Molecules", John Wiley and Sons, London, 1970.

9. R. Friedel and M. Orchin, "U.V. Spectra of Aromatic Compounds", John Wiley, New York, 1951.

10. T. J. Porro, R. E. Anacreon, P.S. Flandreau, and I.S. Fagerson, J. of AOAC, 56, 607, (1973).

11. L. Lang, "Absorption Spectra in UV and Visible Region", Academic Press, New York, Vol. 1, 1961.

12. E. Sawicki, W. Elbert, T. W. Stanley, T. R. Hauser, and F. T. Fox, Anal. Chem., 32, 813 (1960).

13. M. A. Fox and S. W. Staley, Anal. Chem., 48, 997, (1976).

14. L. Lang, "Absorption Spectra in UV and Visible Region", Academic Press, New York, Volume 4, 1961.

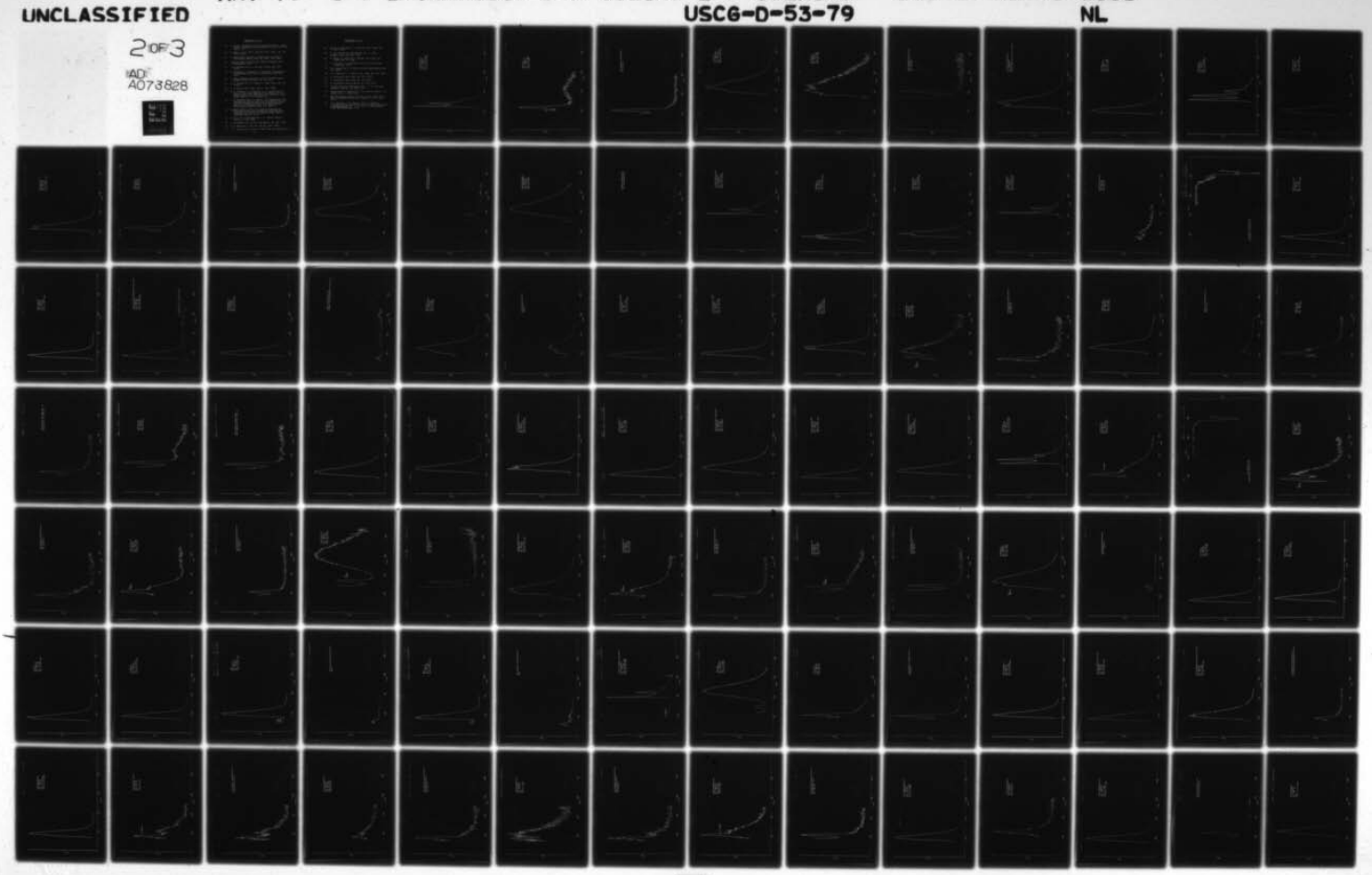
15. G. Guilbault, "Practical Fluorescence", Marcel Dekker, New York, 1973.

16. "Sadtler Index of Fluorescence Spectra", Sadtler Research Labs, Philadelphia, 1974, Volumes 1 & 2.

17. B. Tebbens, "Symposium on Air Pollution Measurements Methods", ASTM Special Tech. Publ., #352, Philadelphia, 1963, p.17.

AD-A073 828 BAIRD CORP BEDFORD MA GOVERNMENT SYSTEMS DIV F/G 7/2
A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS,(U)
MAY 79 J T BROWNRIGG, D A BUSCH, L P GIERING DOT-CG-81-78-1888
UNCLASSIFIED USCG-D-53-79 NL

2 OF 3
AD A073828



REFERENCES (con't)

18. G. Schenk, "Absorption of Light and UV Radiation: Fluorescence and Phosphorescence Emission", Allyn and Bacon, Boston, 1973.

19. H. Davis, L. Lee, and T. Davidson, Anal. Chem., 38, (12) 1752, (1966).

20. G. Renkes and F. Weltack, "Fluorescence of Acetone in the Solution Phase", JACS, 91, (26), 7514 (1969).

21. "Sadtler Index of UV Spectra", Sadtler Research Labs., Philadelphia, 1960.

22. J. W. Bridges and R. T. Williams, Nature, 196, 4849 (1962).

23. G. Barenboim, A. Domanskii, K. Turoveror, "Luminescence of Biopolymers and Cells", Plenum Press, New York, 1969.

24. L. Lang, "Absorption Spectra in UV and Visible Region", Academic Press, New York, Vol. #6, 1961.

25. R. F. Borkman and D. R. Kearns, J. Chem. Phys., 44, 945, (1966).

26. C. A. Parker, Anal. Chem., 34 (4), 502, (1962).

27. B. R. Chisholm, H. G. Eldering, L. P. Giering and A. W. Hornig, "Total Luminescence Contour Spectra of Six Topped Crude Oils", ERDA Technical Information Center Report BERC/RI-76/16, November 1976.

28. J. T. Brownrigg and A. W. Hornig, "Low Temperature Total Luminescence Contour Spectra of Six Topped Crude Oils and Their Vacuum Distillate and Residuum Fractions", Technical Information Center, U.S. Department of Energy Report, BETC/RI-78/13, July 1978.

29. "Standard Method of Test for Spectral Bandwidth and Wavelength Accuracy of Fluorescence Spectrometers", ASTM Designation E388-72, ASTM 1975 Annual Book of Standards, Part 42, p.303.

30. R. Stain, W. E. Schneider and J. K. Jackson, Applied Optics, 2, 1151 (1963).

31. J. Yguerabide, Rev. of Sci. Instruments, 39, 1048 (1968).

32. W. H. Melhuish, J. Opt. Soc. Am. 52, 1256, (1962).

33. J. S. Brinen and B. Singh, J. Amer. Chem. Soc. 93,6623(1971).

REFERENCES (con't)

34. Charles D. Ford and R. J. Hurtubise, Anal. Chem., 50, 610, (1978).

35. E. Clar "Polycyclic Hydrocarbons" Vol. 1, p.94, Academic Press, New York 1964.

36. N. Matoga, Y. Kaifu and M. Koezumi, Bull. Chem. Soc. Japan, 29, 373 (1956).

37. V. N. Mallet, P.E. Belliveau and R. W. Free, Residue Review 59, (1975).

38. T.H. Edwards and P. D. Wilson, Applied Spectroscopy, 28 541 (1974).

39. C. G. Enke and T. A. Nunian, Anal. Chem. 48, 705A (1976).

40. T. Hirschfeld, Anal. Chem. 50, 1023 (1978).

41. T. Hirschfeld, Anal. Chem. 50, 1225 (1978).

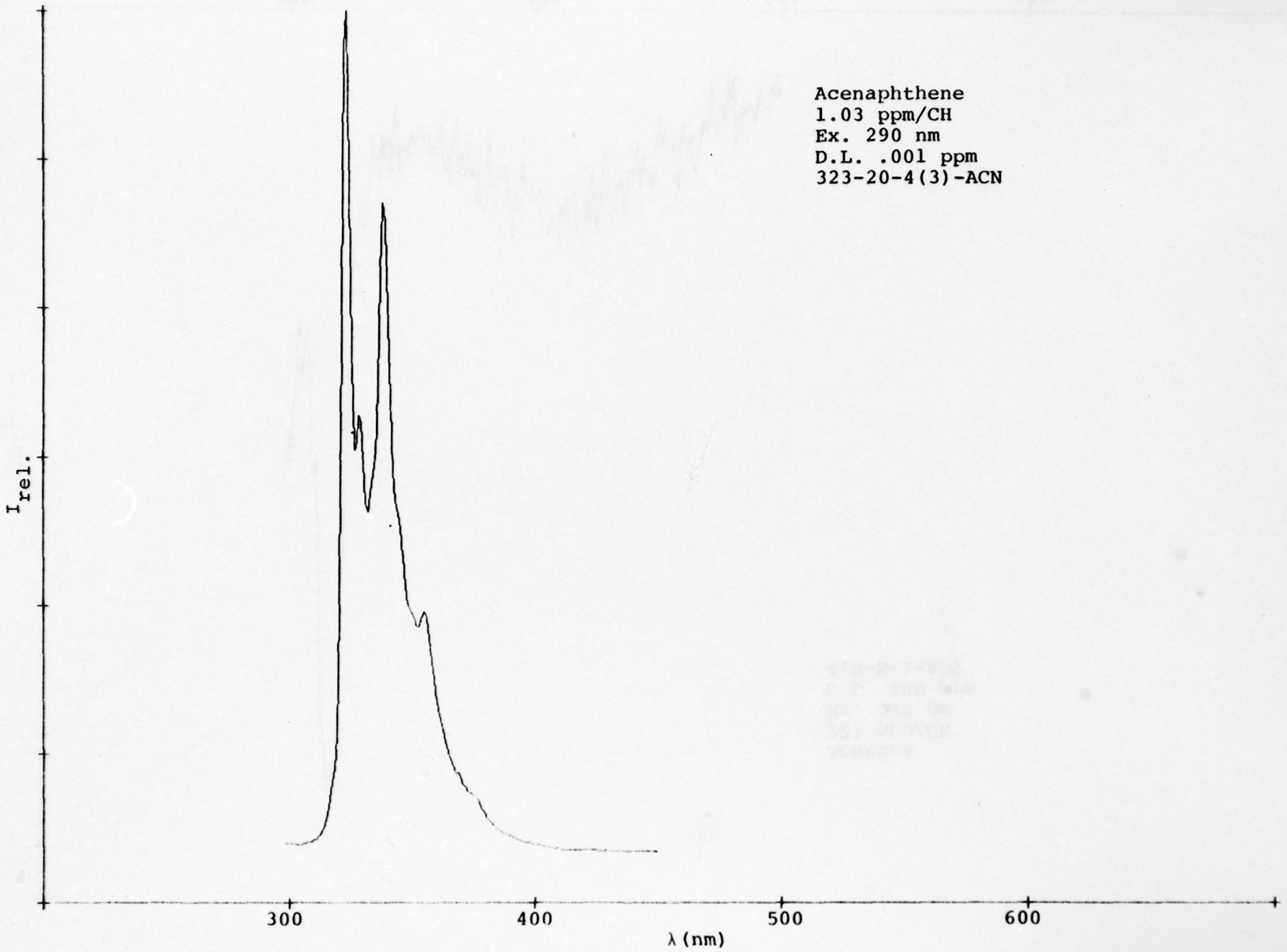
42. T. Hirschfeld, Applied Optics, 17, 1400 (1978).

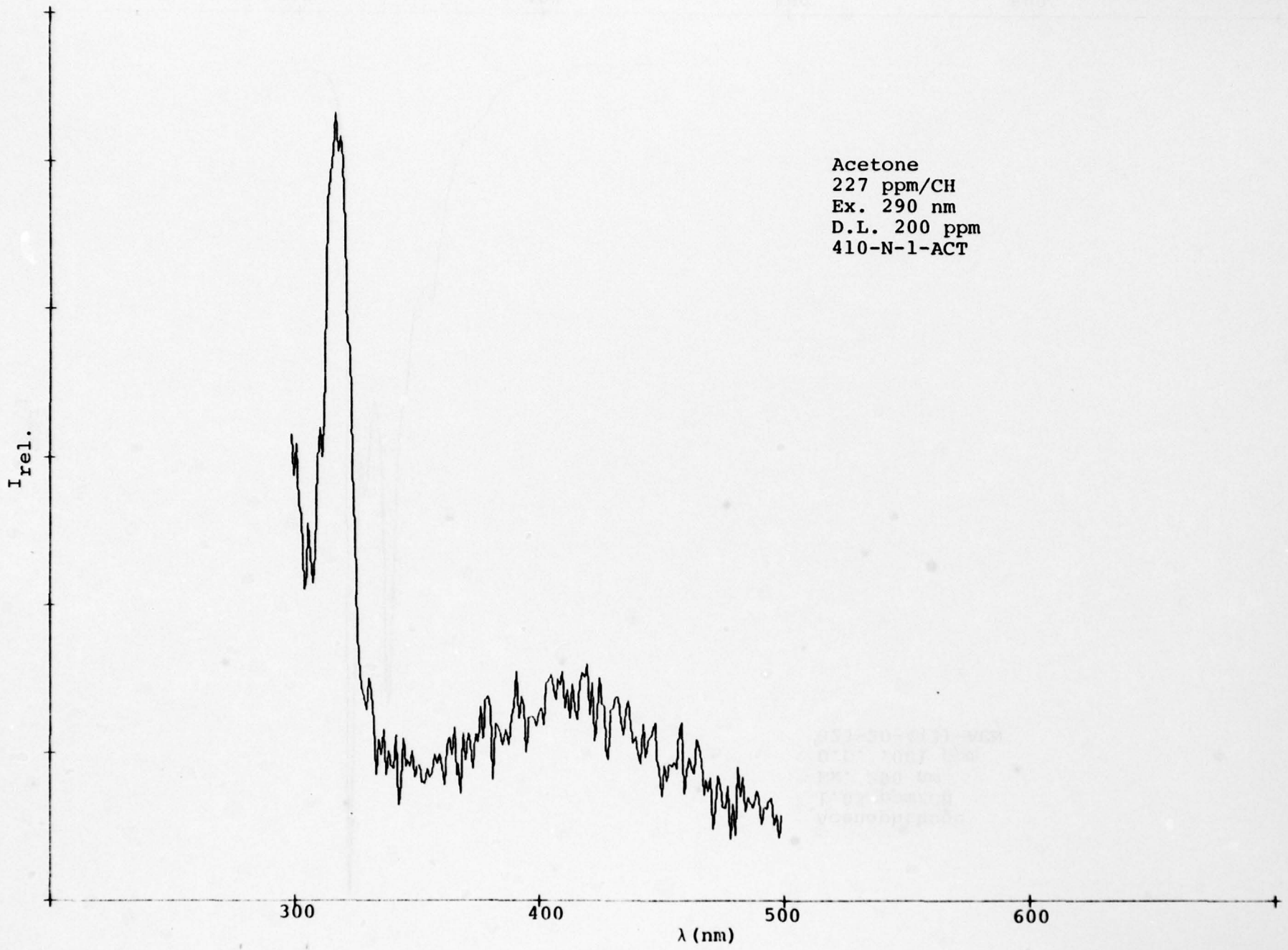
43. "Organic Molecular Photophysics" Vol. 1 & 2, John Wiley and Sons, Lord ed. J.B. Birks 1975.

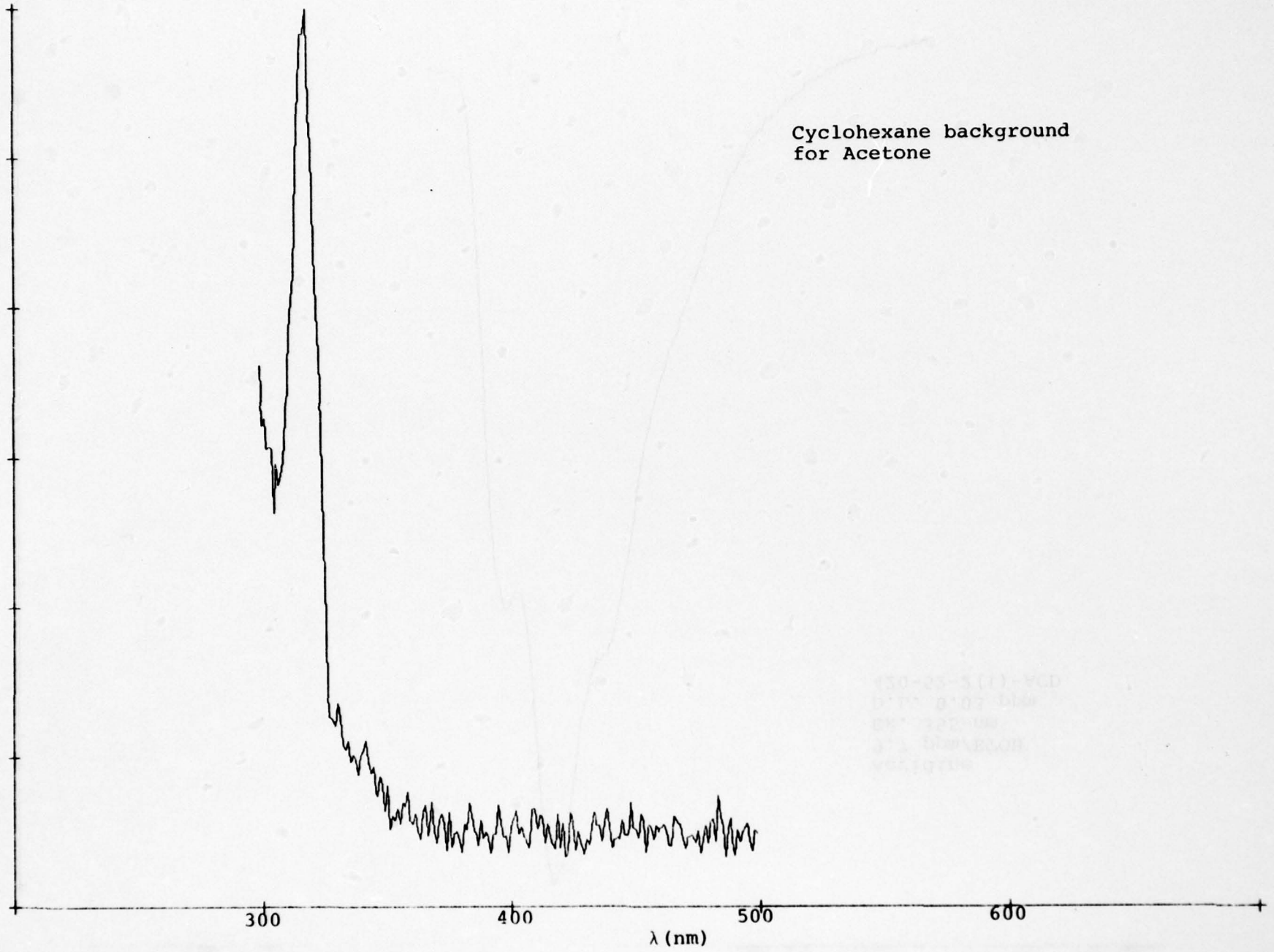
44. "Luminescence in Chemistry" D. Van Nostrand Company, Ltd. London, ed. E. J. Bowen 1968.

45. MTP International Review of Science, Anal. Chem. Part 1, Physical Chemistry Series One, Volume 12 ed. T.S. West 1973.

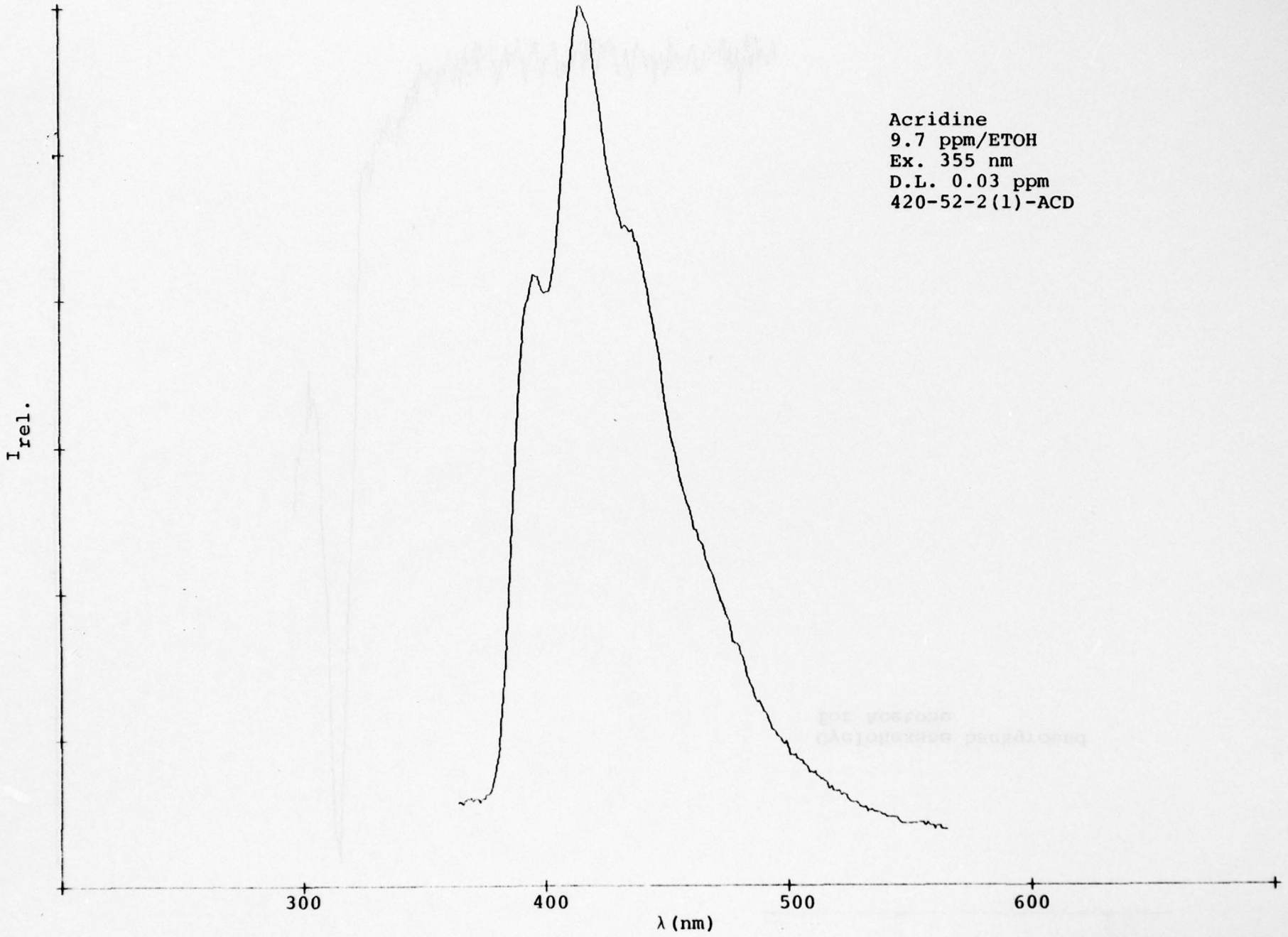
46. C. J. Seliskar, O. S. Khalili, and S. P. McGlynn, "Luminescence Characteristics of Polar Aromatic Molecules", in Excited States, Vol. I, ed. by E. C. Lim, Academic Press, New York-London, 1974.

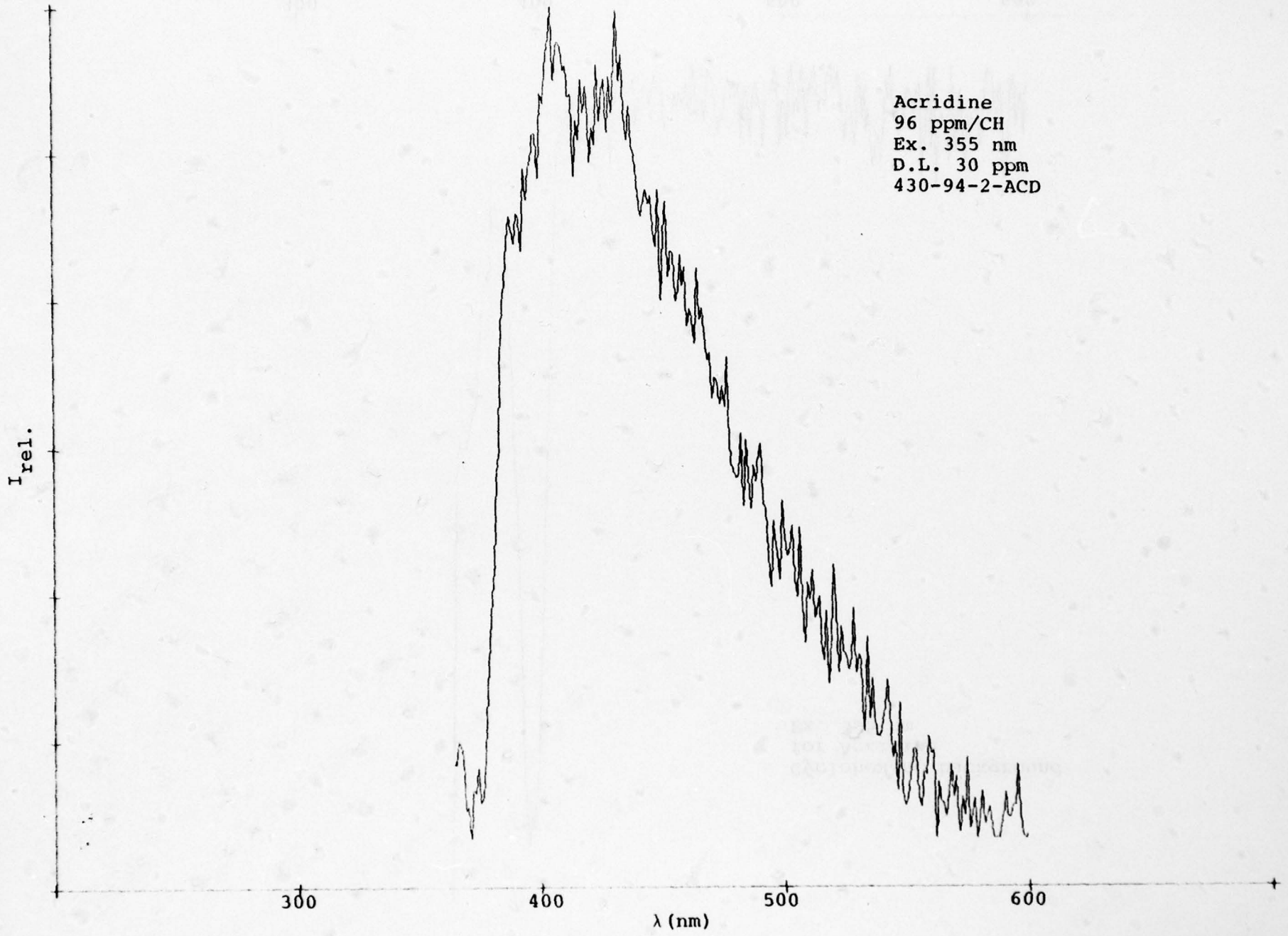

Acenaphthene
1.03 ppm/CH
Ex. 290 nm
D.L. .001 ppm
323-20-4(3)-ACN
I rel.
300
400
500
600
λ (nm)

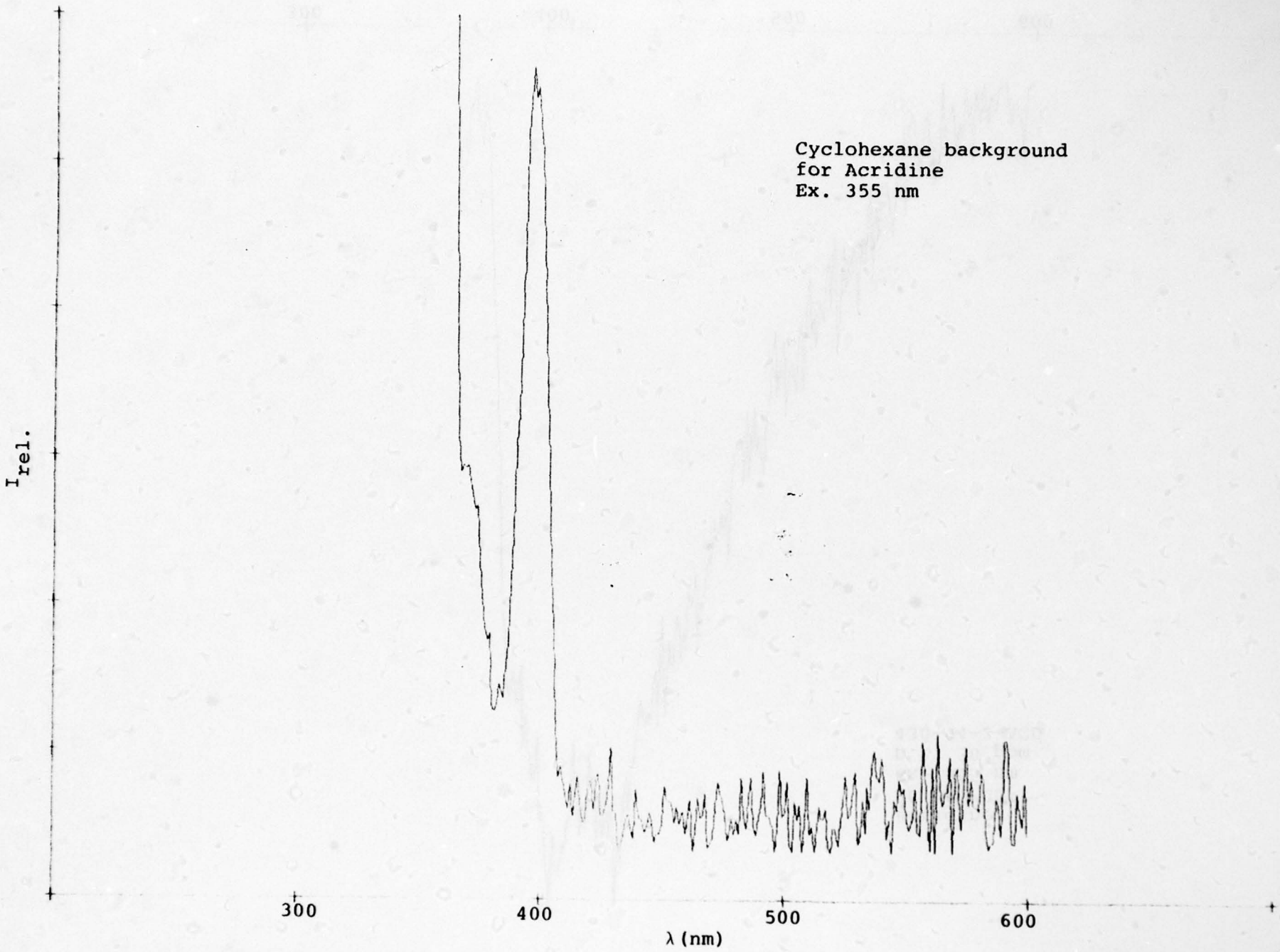

Acetone
227 ppm/CH
Ex. 290 nm
D.L. 200 ppm
410-N-1-ACT
$I_{rel.}$
300
400
500
600
λ (nm)



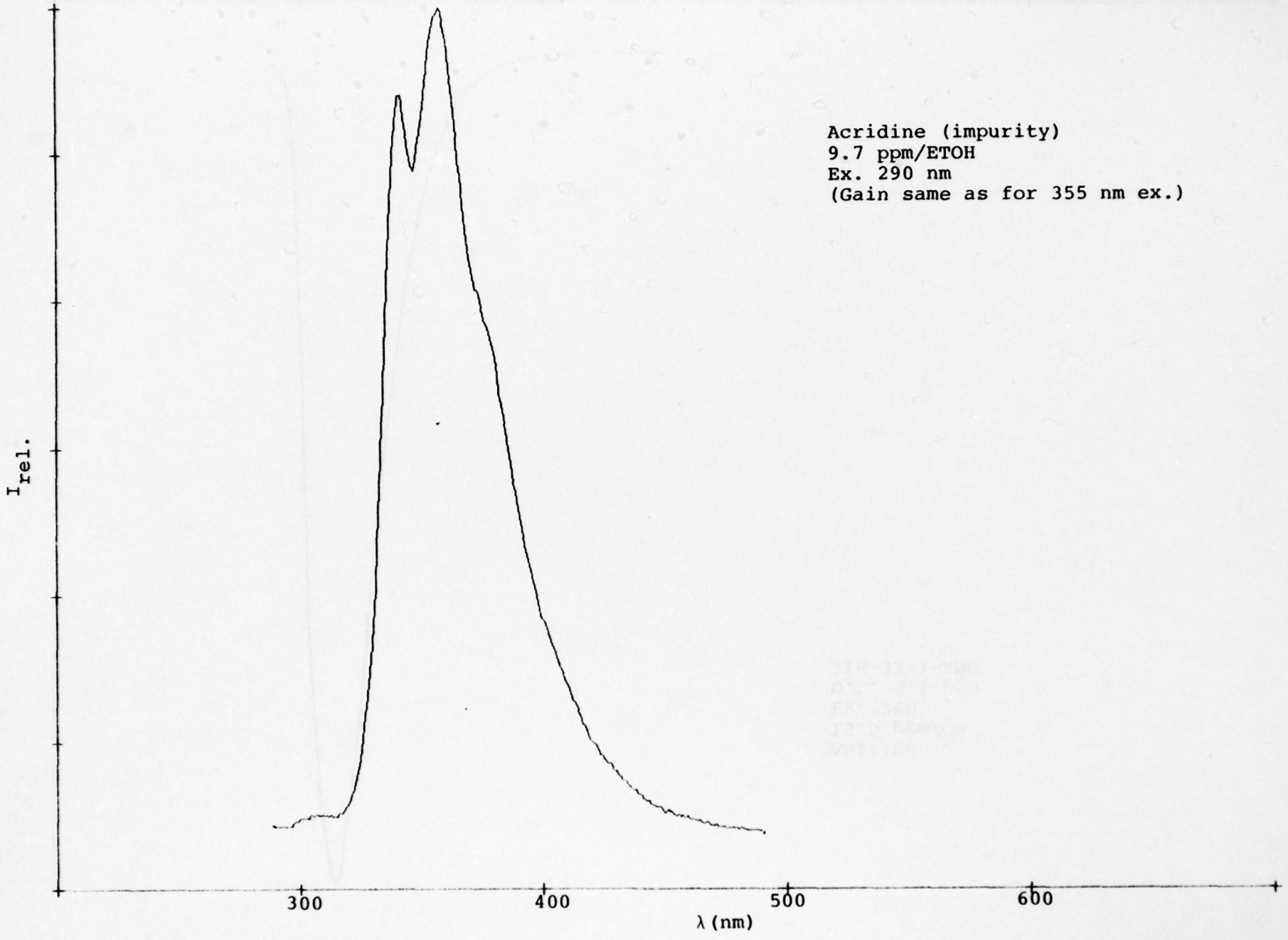
Cyclohexane background
for Acetone

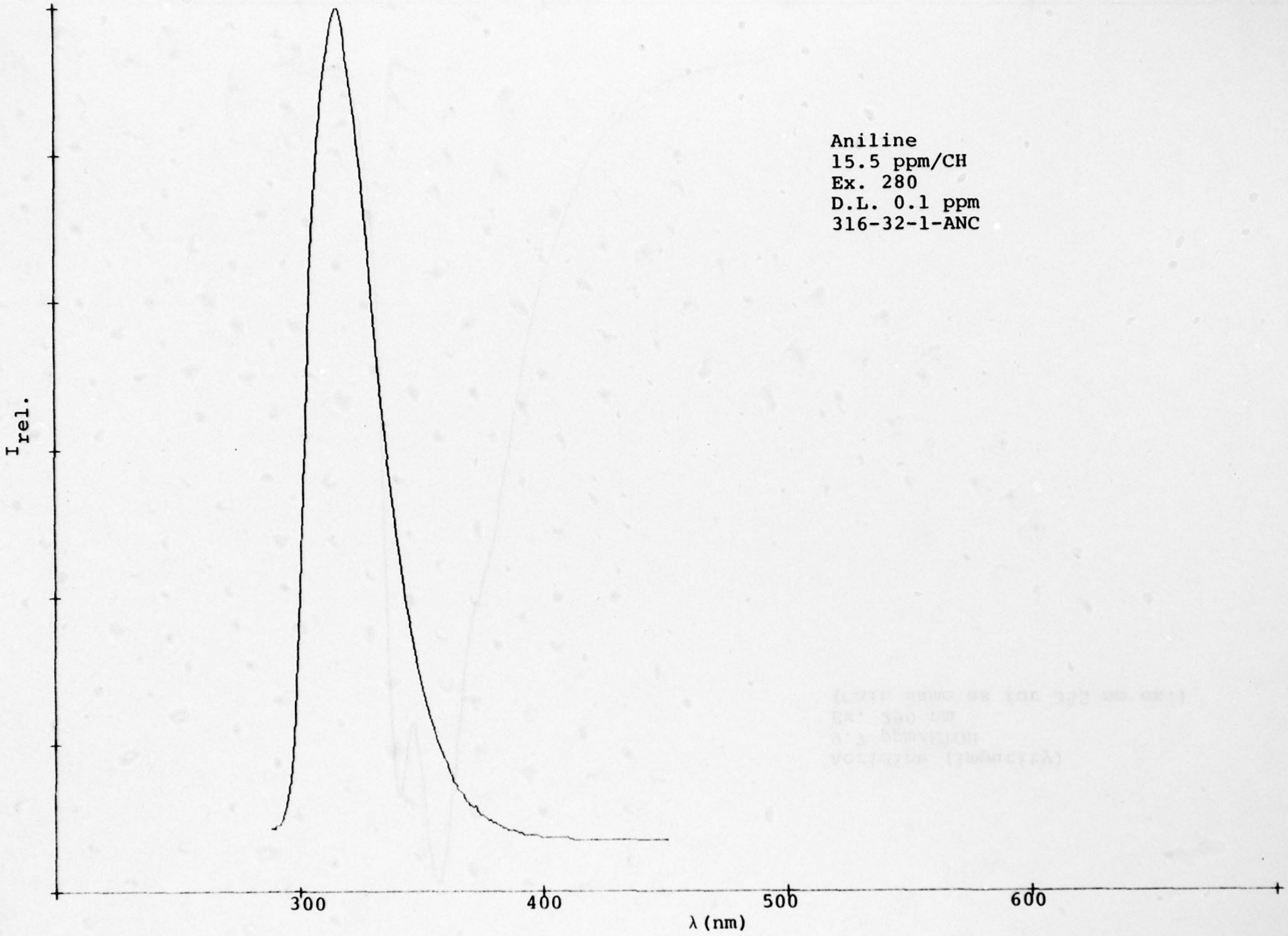

Acridine
9.7 ppm/ETOH
Ex. 355 nm
D.L. 0.03 ppm
420-52-2(1)-ACD
I rel.
300
400
500
600
λ (nm)

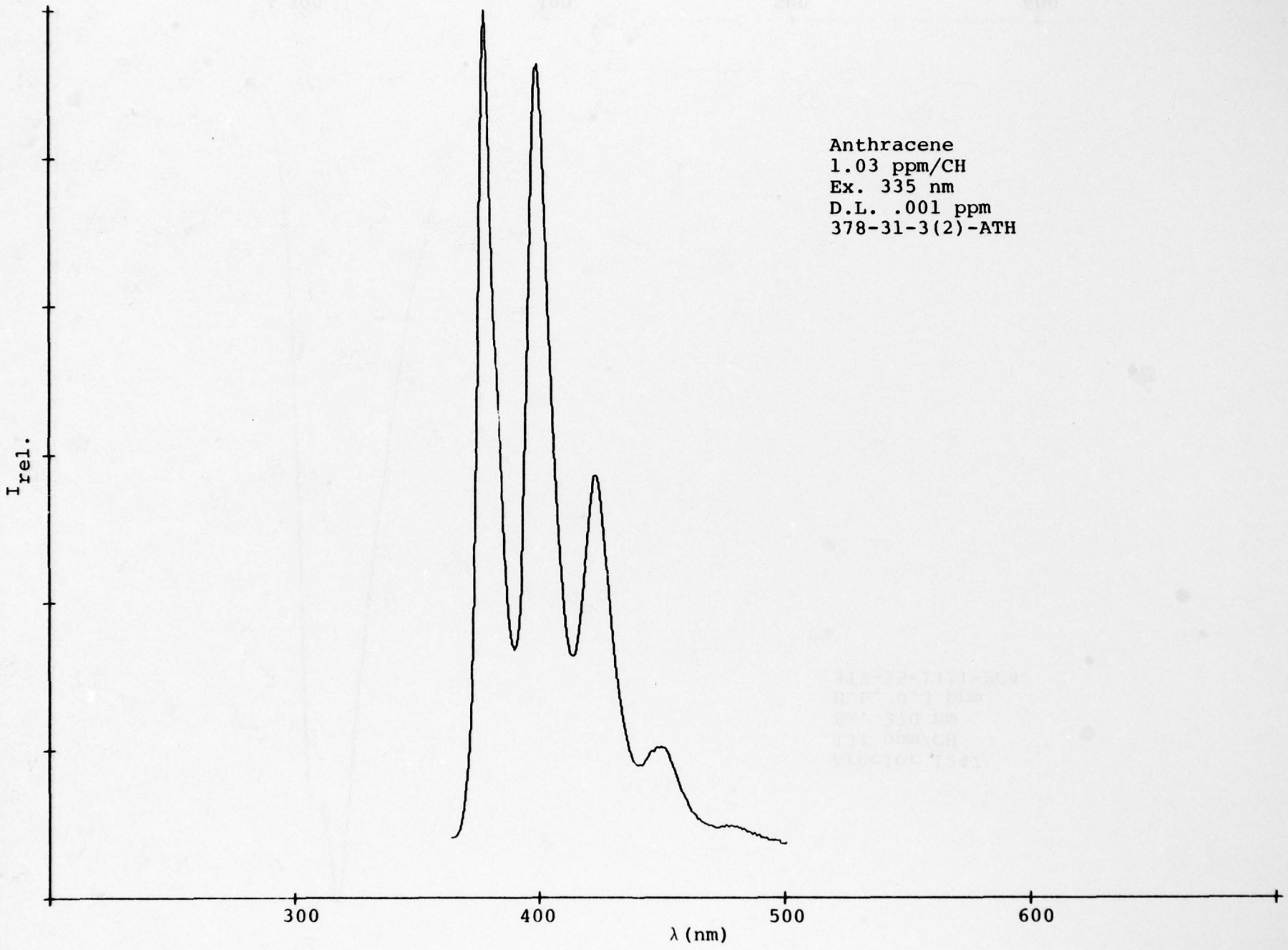

Acridine
96 ppm/CH
Ex. 355 nm
D.L. 30 ppm
430-94-2-ACD
$I_{rel.}$
300
400
500
600
λ (nm)

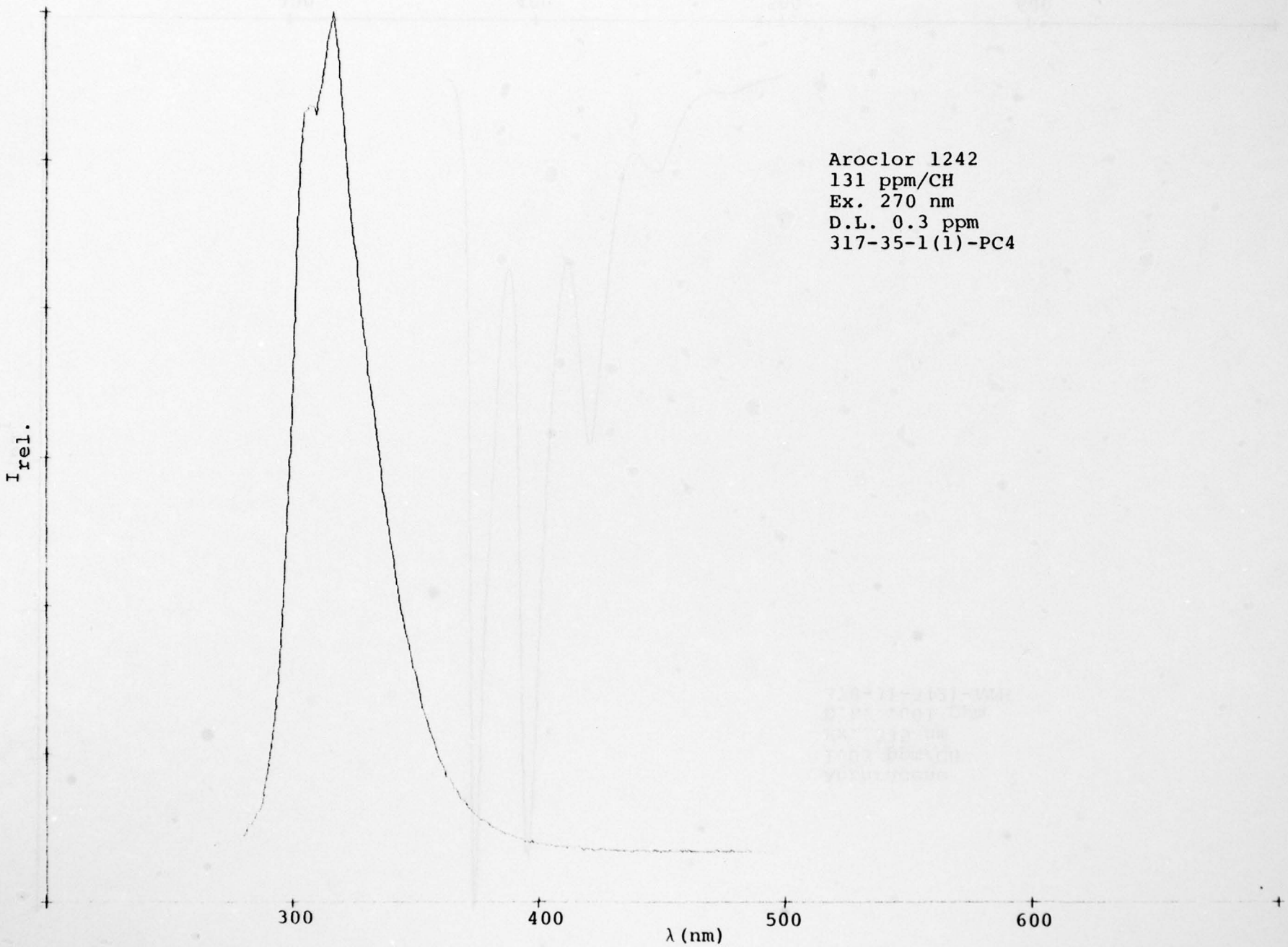

Cyclohexane background
for Acridine
Ex. 355 nm
$I_{rel.}$
300
400
500
600
λ (nm)

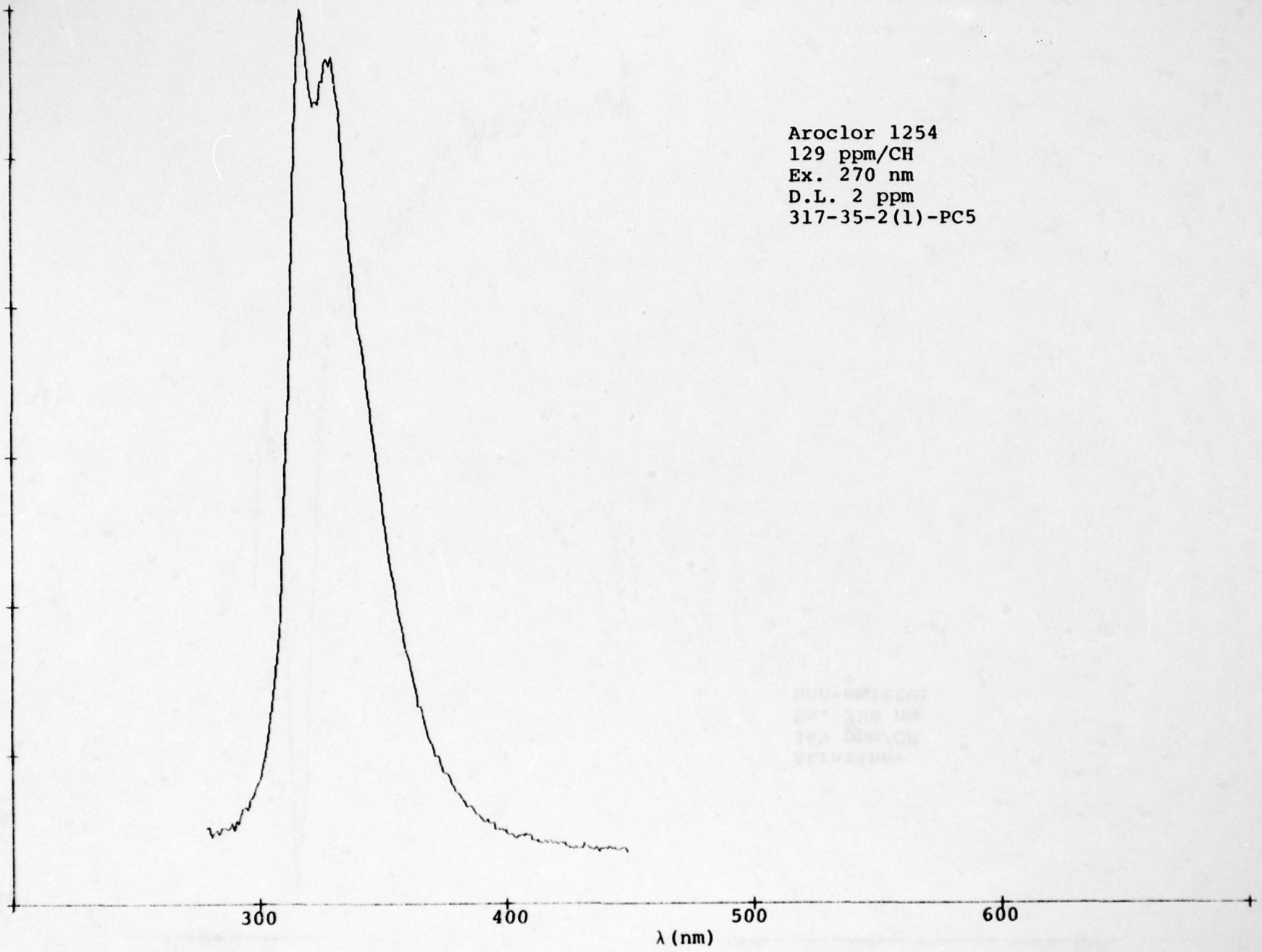
N=17

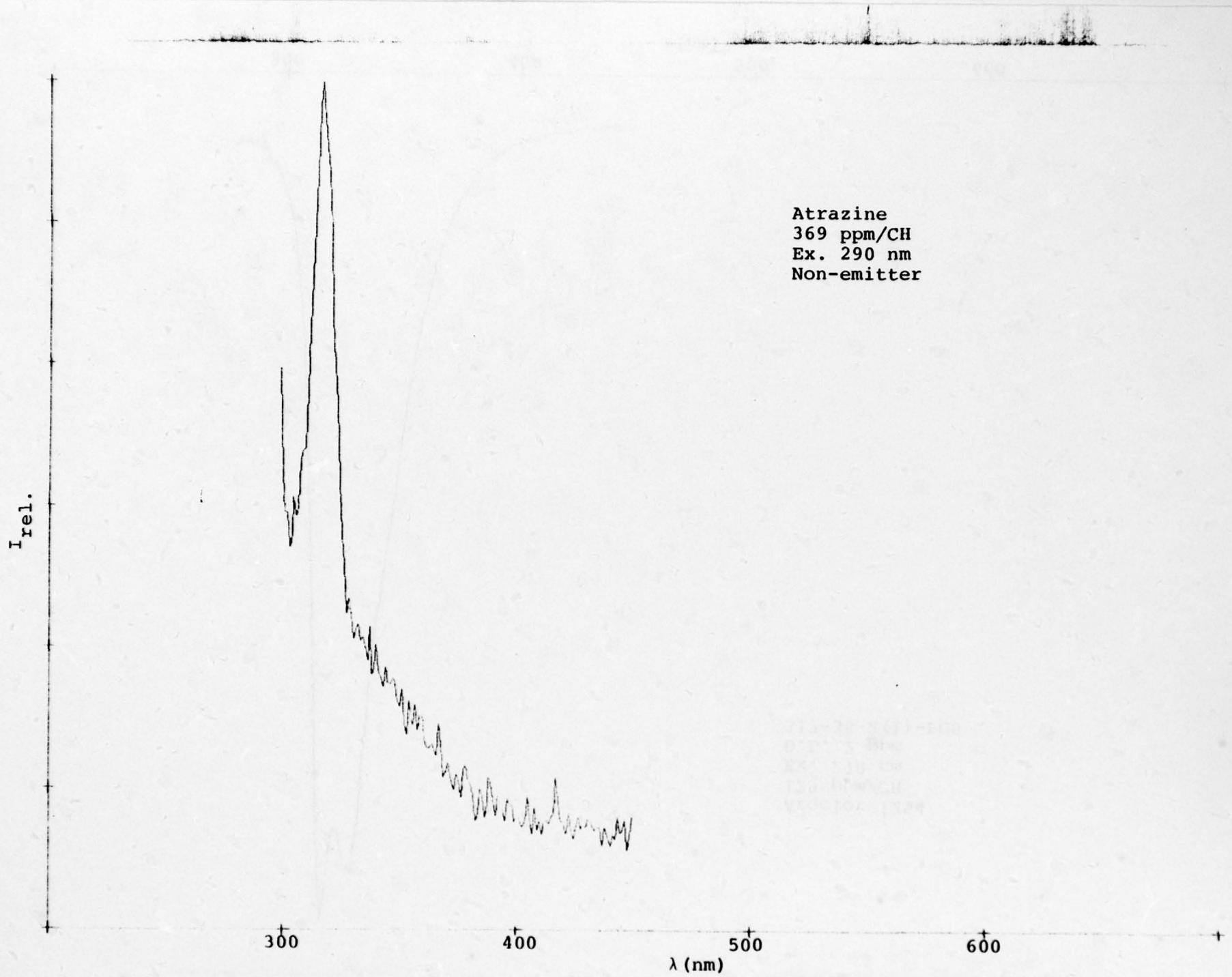

Acridine (impurity)
9.7 ppm/ETOH
Ex. 290 nm
(Gain same as for 355 nm ex.)
$I_{rel.}$
300
400
500
600
λ (nm)

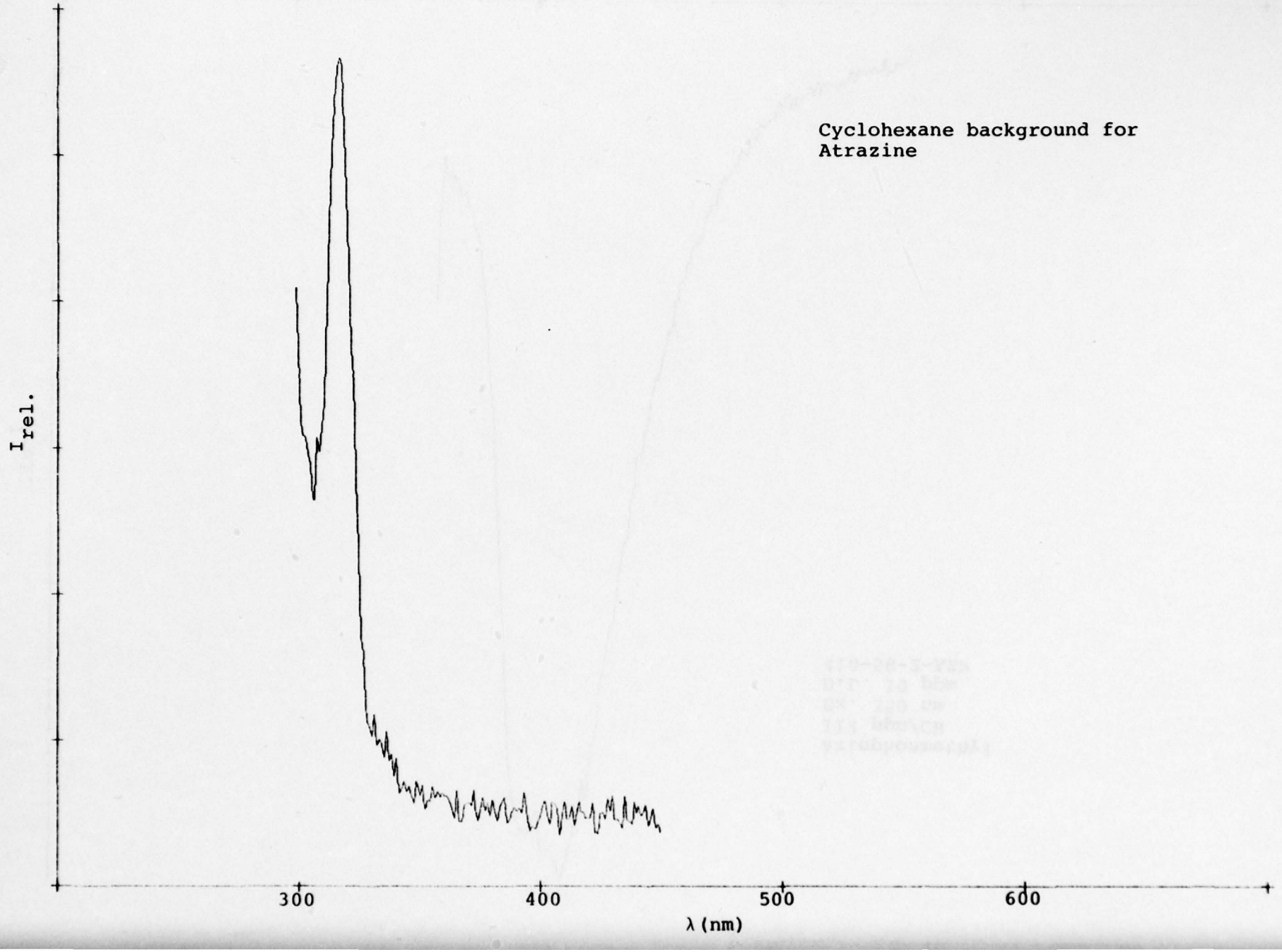

Aniline
15.5 ppm/CH
Ex. 280
D.L. 0.1 ppm
316-32-1-ANC
$I_{rel.}$
300
400
500
600
λ (nm)

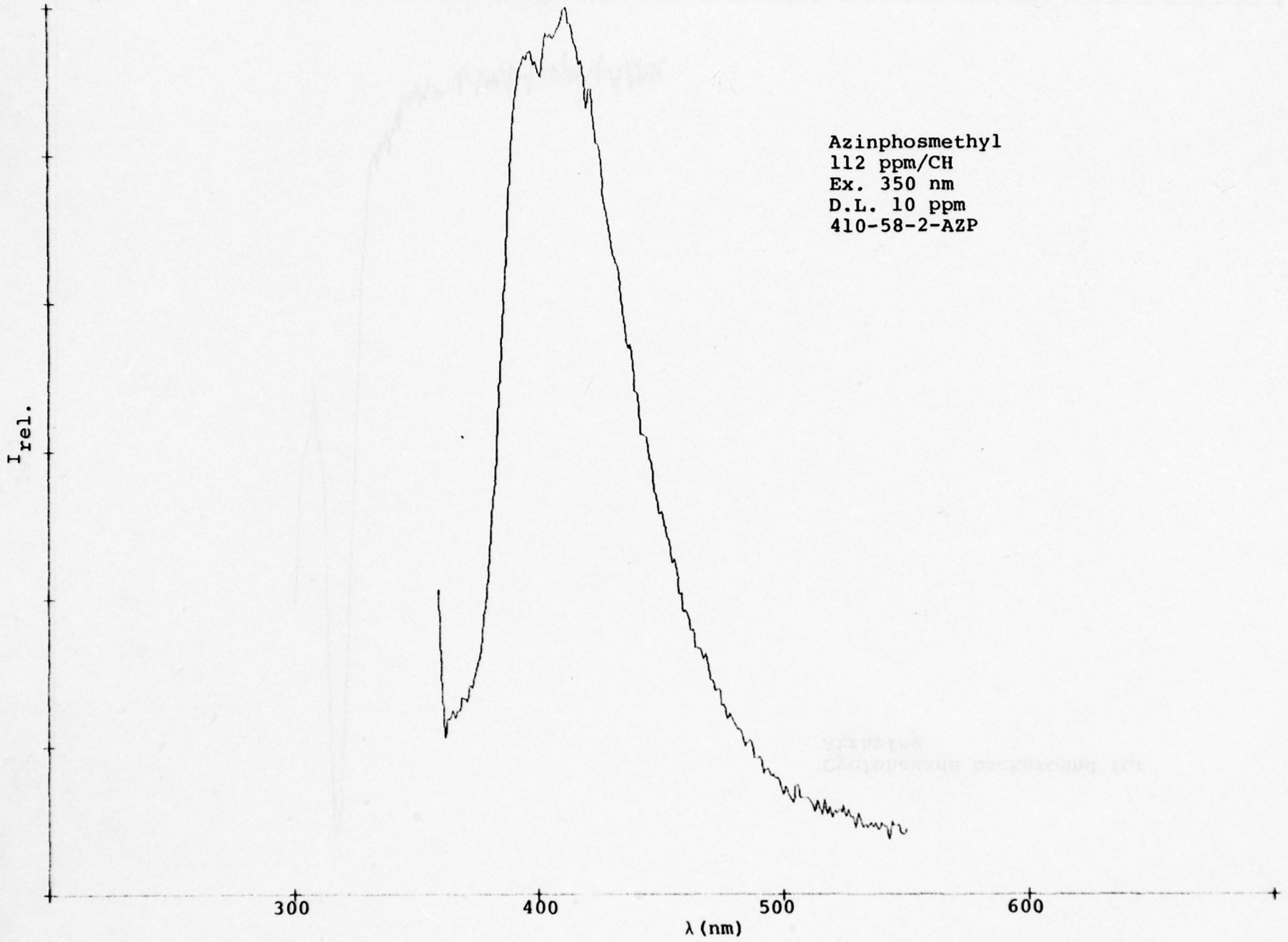

Anthracene
1.03 ppm/CH
Ex. 335 nm
D.L. .001 ppm
378-31-3(2)-ATH
$I_{rel.}$
300
400
500
600
λ (nm)


Aroclor 1242
131 ppm/CH
Ex. 270 nm
D.L. 0.3 ppm
317-35-1(1)-PC4
$I_{rel.}$
300
400
500
600
λ (nm)

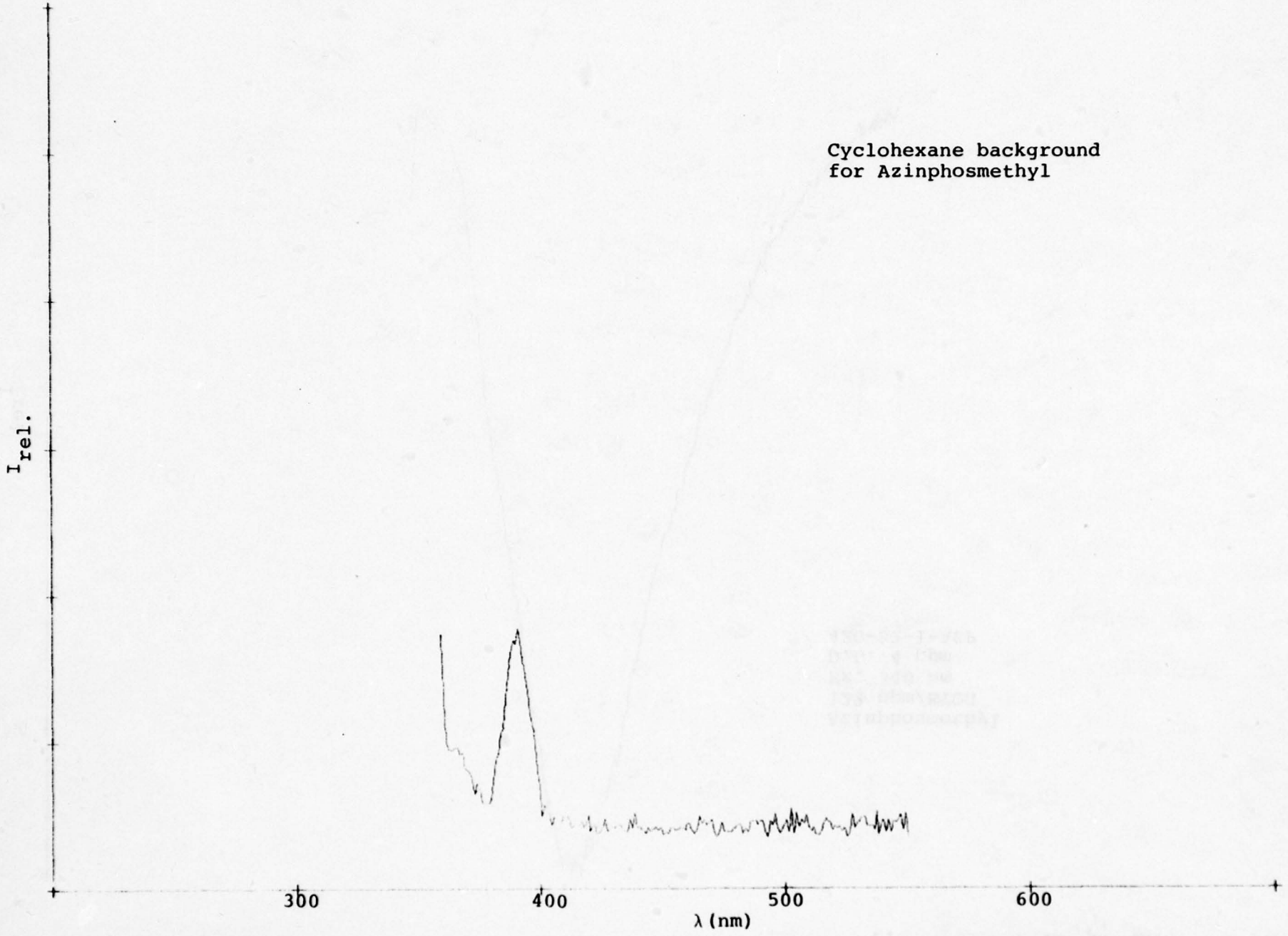

Aroclor 1254
129 ppm/CH
Ex. 270 nm
D.L. 2 ppm
317-35-2(1)-PC5
300
400
500
600
λ (nm)

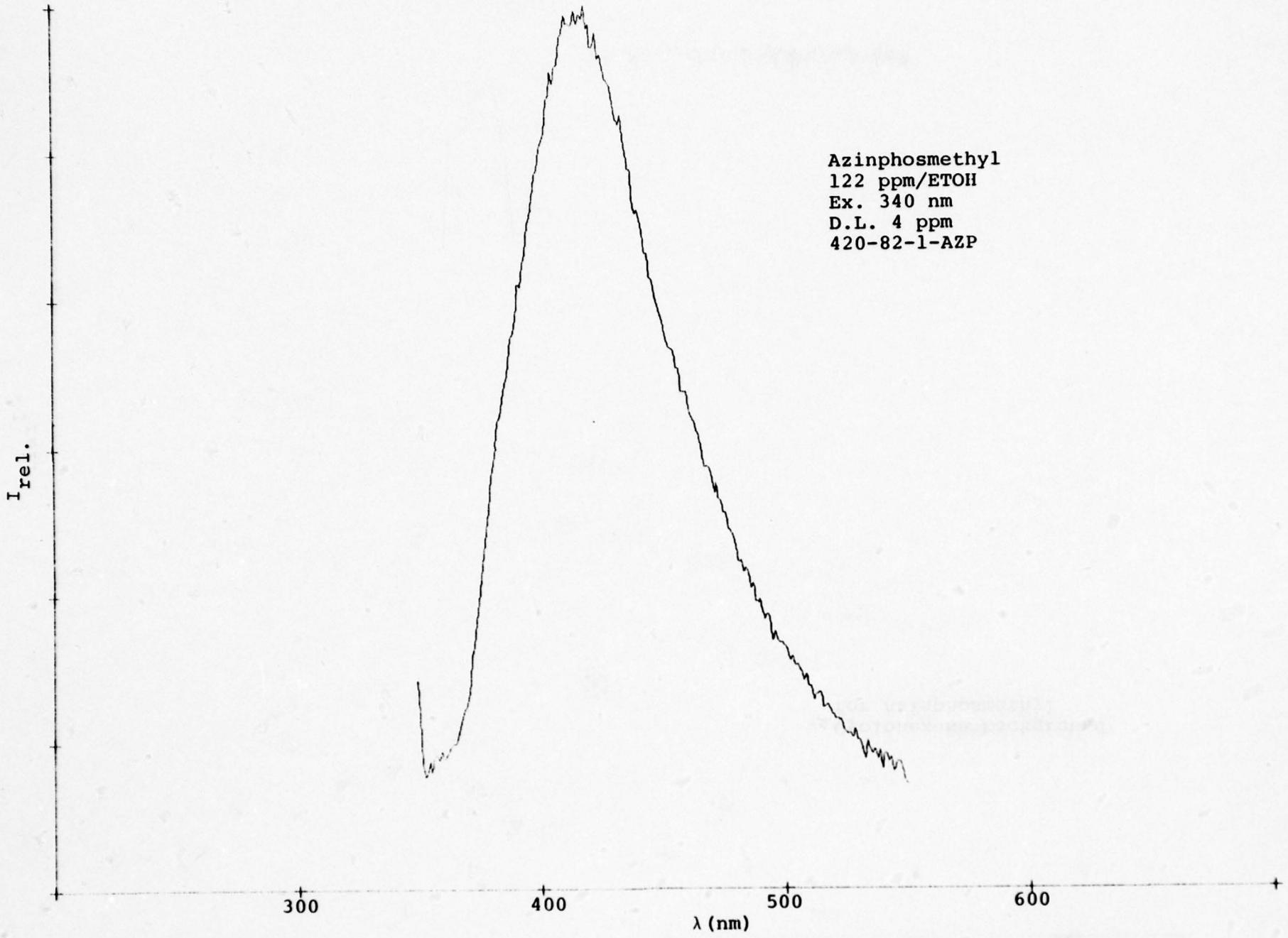

Atrazine
369 ppm/CH
Ex. 290 nm
Non-emitter
$I_{rel.}$
300
400
500
600
λ (nm)


Cyclohexane background for
Atrazine
$I_{rel.}$
300
400
500
600
λ (nm)

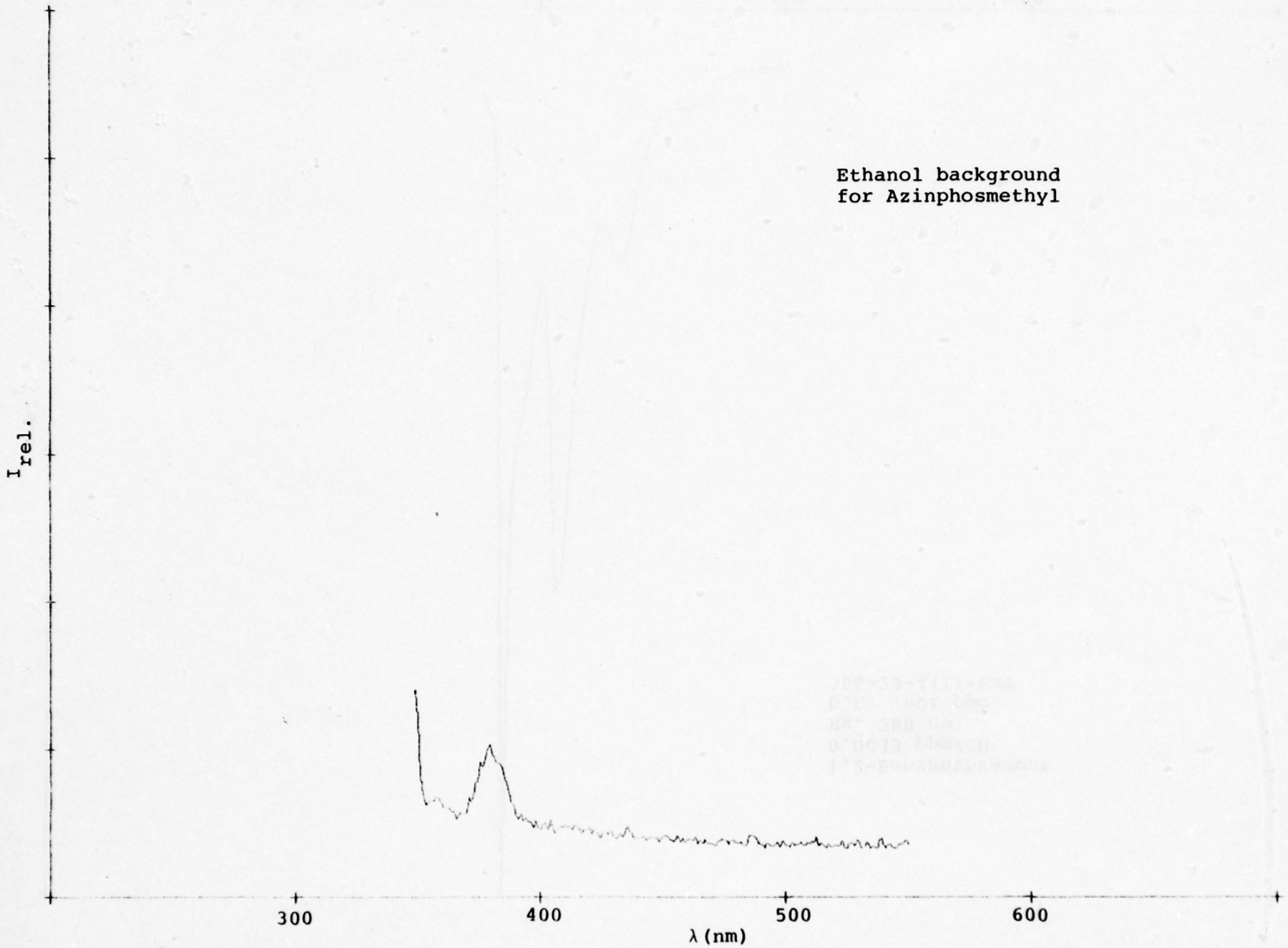

Azinphosmethyl
112 ppm/CH
Ex. 350 nm
D.L. 10 ppm
410-58-2-AZP
$I_{rel.}$
300
400
500
600
λ (nm)

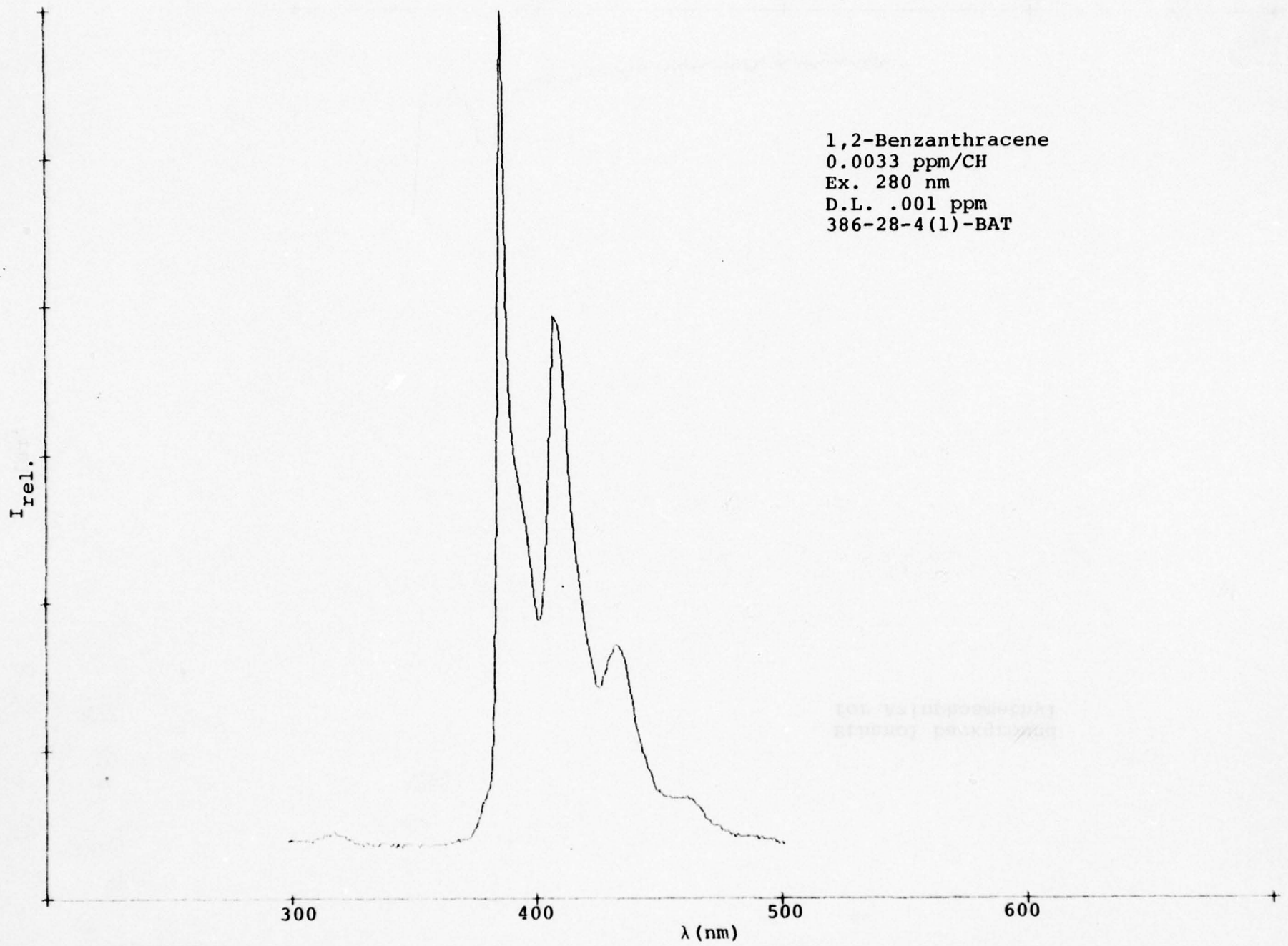
Cyclohexane background
for Azinphosmethyl

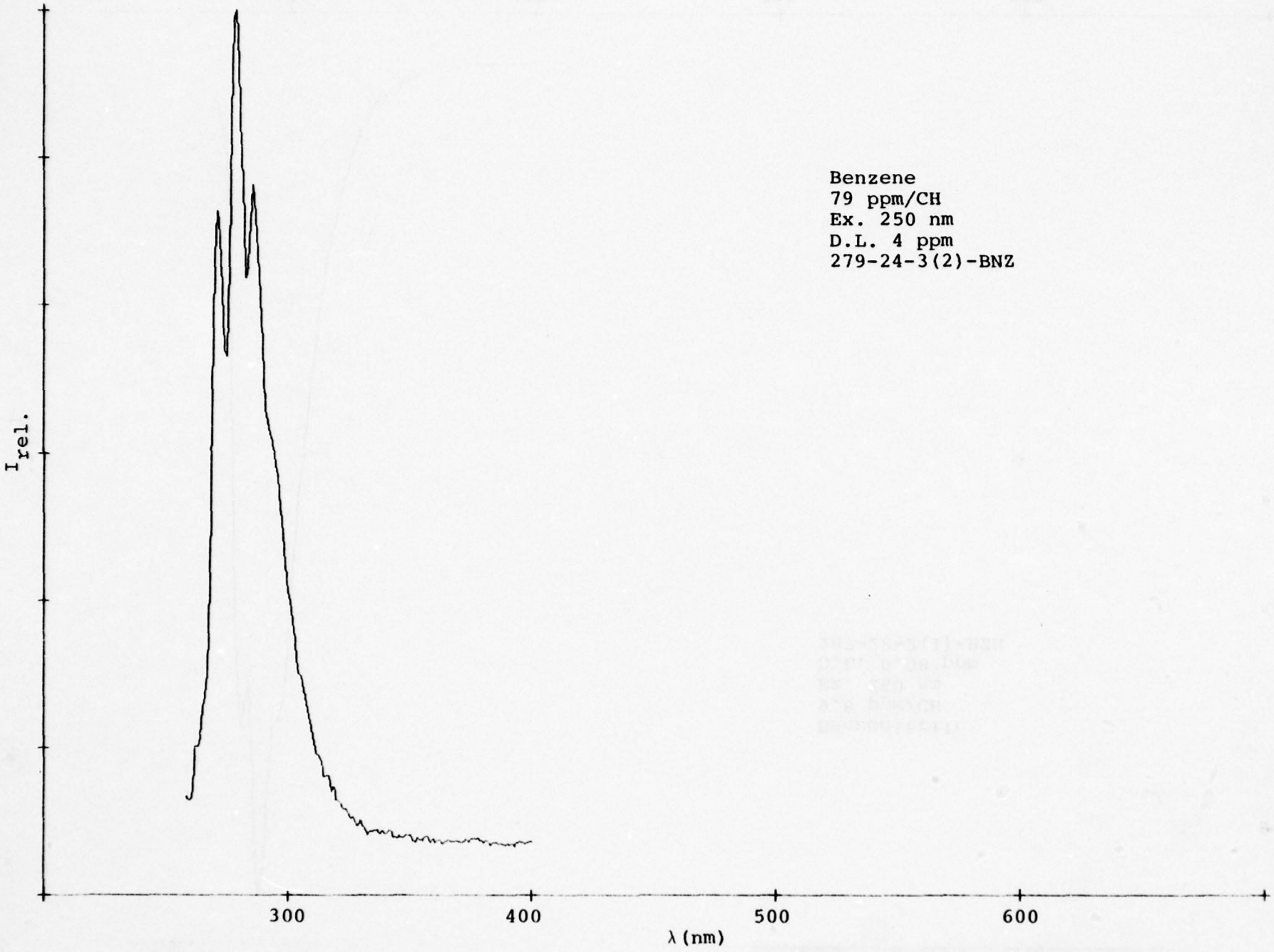


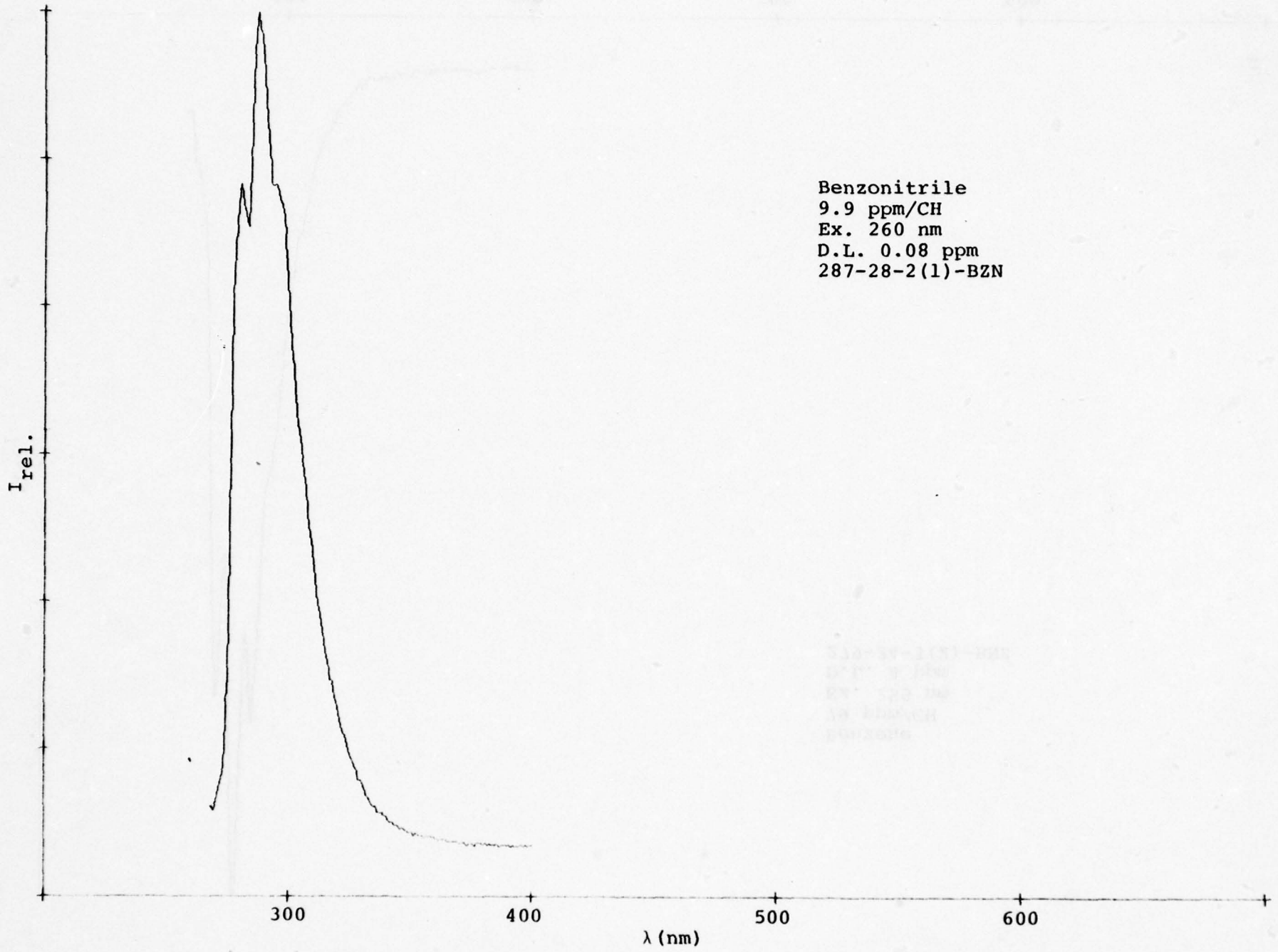

Azinphosmethyl
122 ppm/ETOH
Ex. 340 nm
D.L. 4 ppm
420-82-1-AZP
$I_{rel.}$
300
400
500
600
λ (nm)

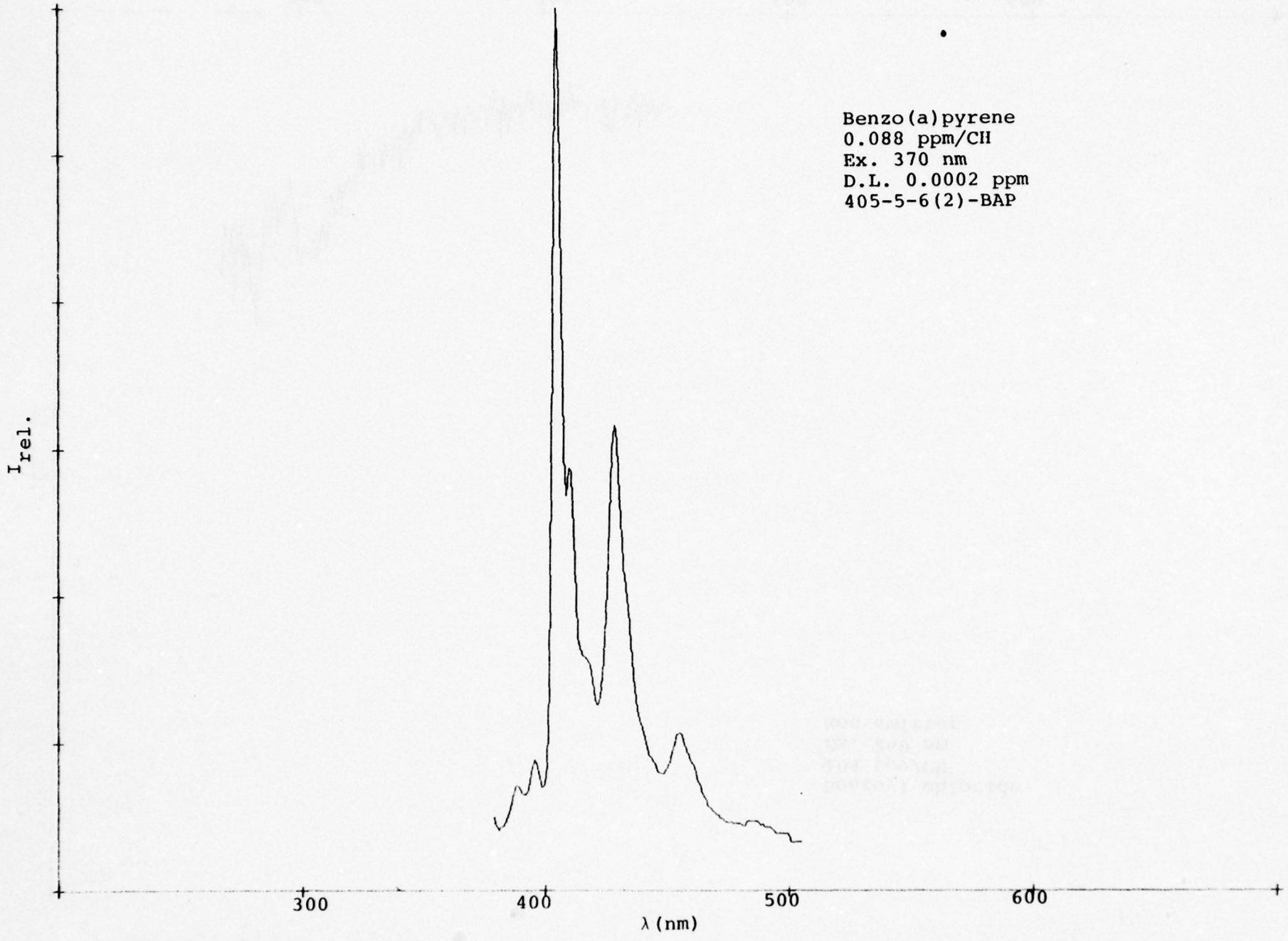
Ethanol background
for Azinphosmethyl

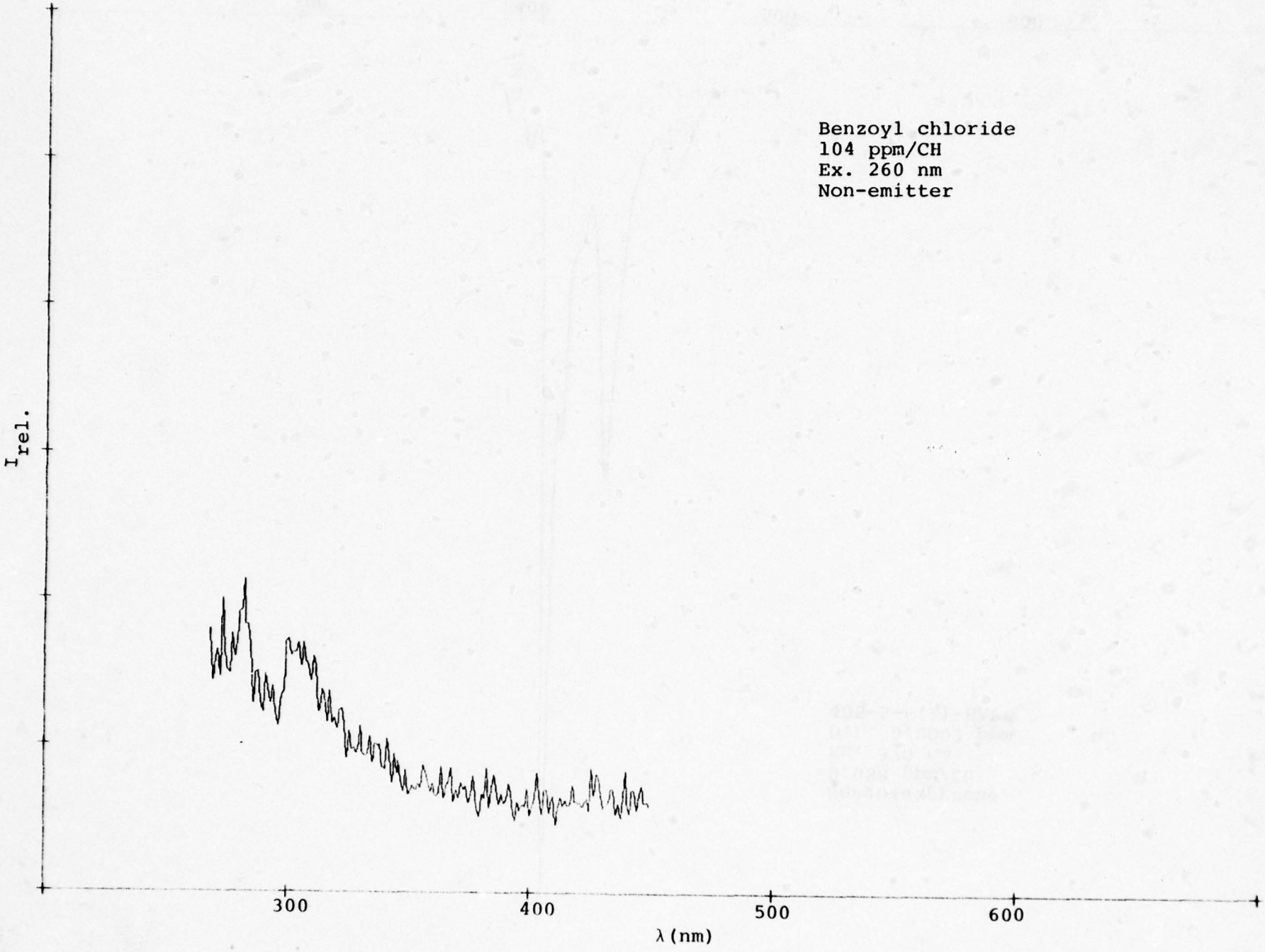


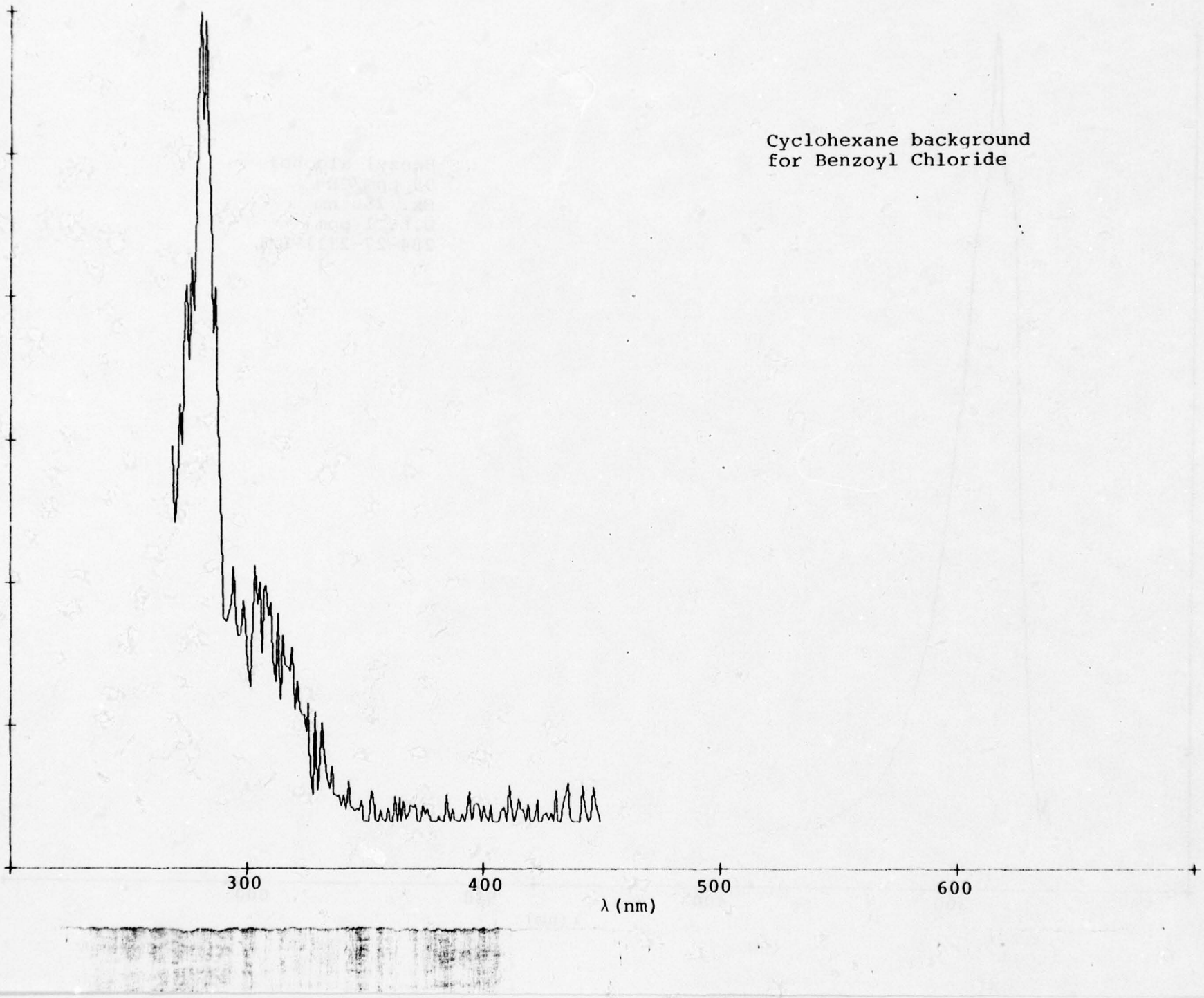

1,2-Benzanthracene
0.0033 ppm/CH
Ex. 280 nm
D.L. .001 ppm
386-28-4(1)-BAT
I rel.
300
400
500
600
λ (nm)


Benzene
79 ppm/CH
Ex. 250 nm
D.L. 4 ppm
279-24-3(2)-BNZ
$I_{rel.}$
300
400
500
600
λ (nm)

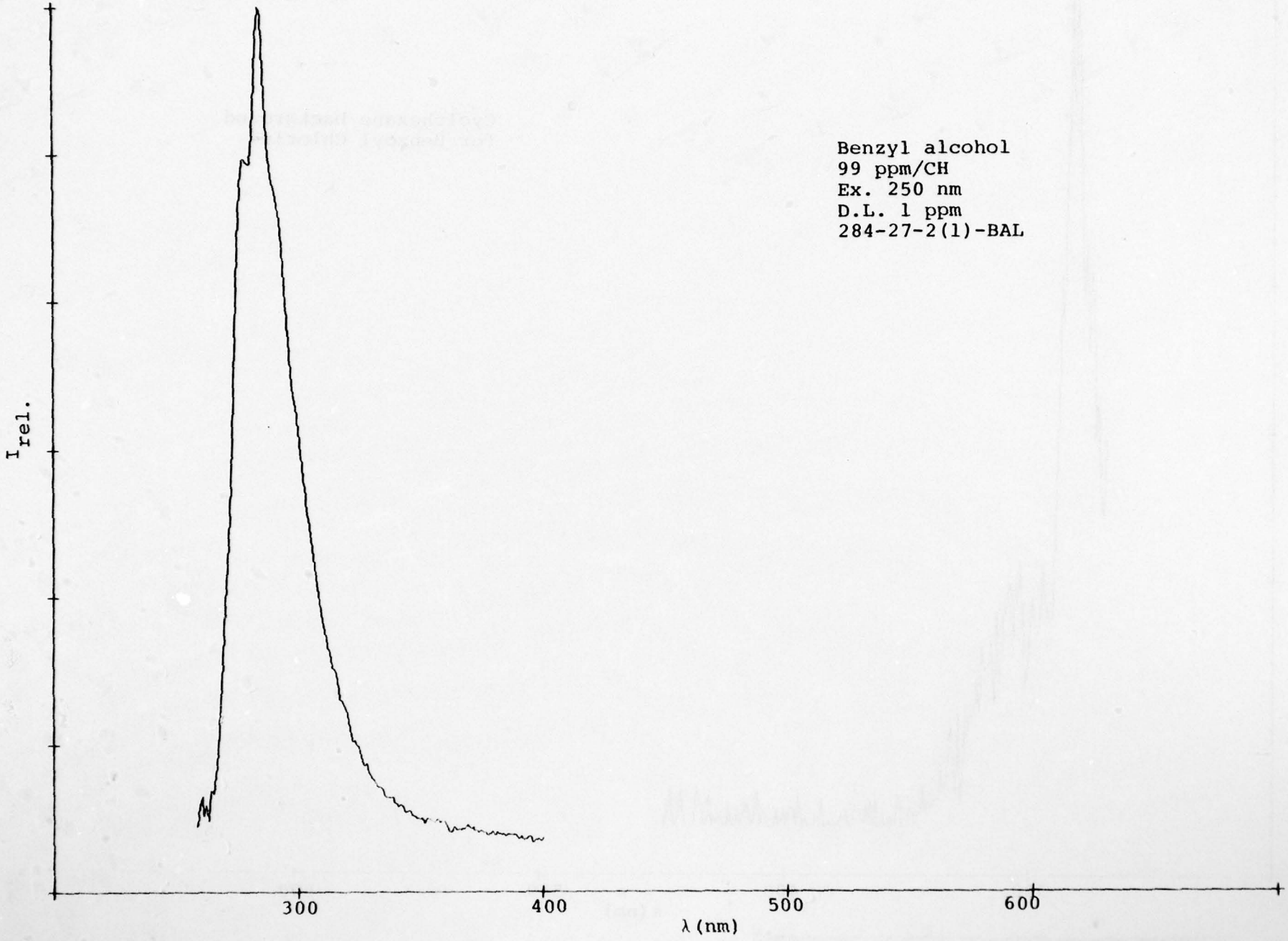

Benzonitrile
9.9 ppm/CH
Ex. 260 nm
D.L. 0.08 ppm
287-28-2(1)-BZN
$I_{rel.}$
300
400
500
600
λ (nm)

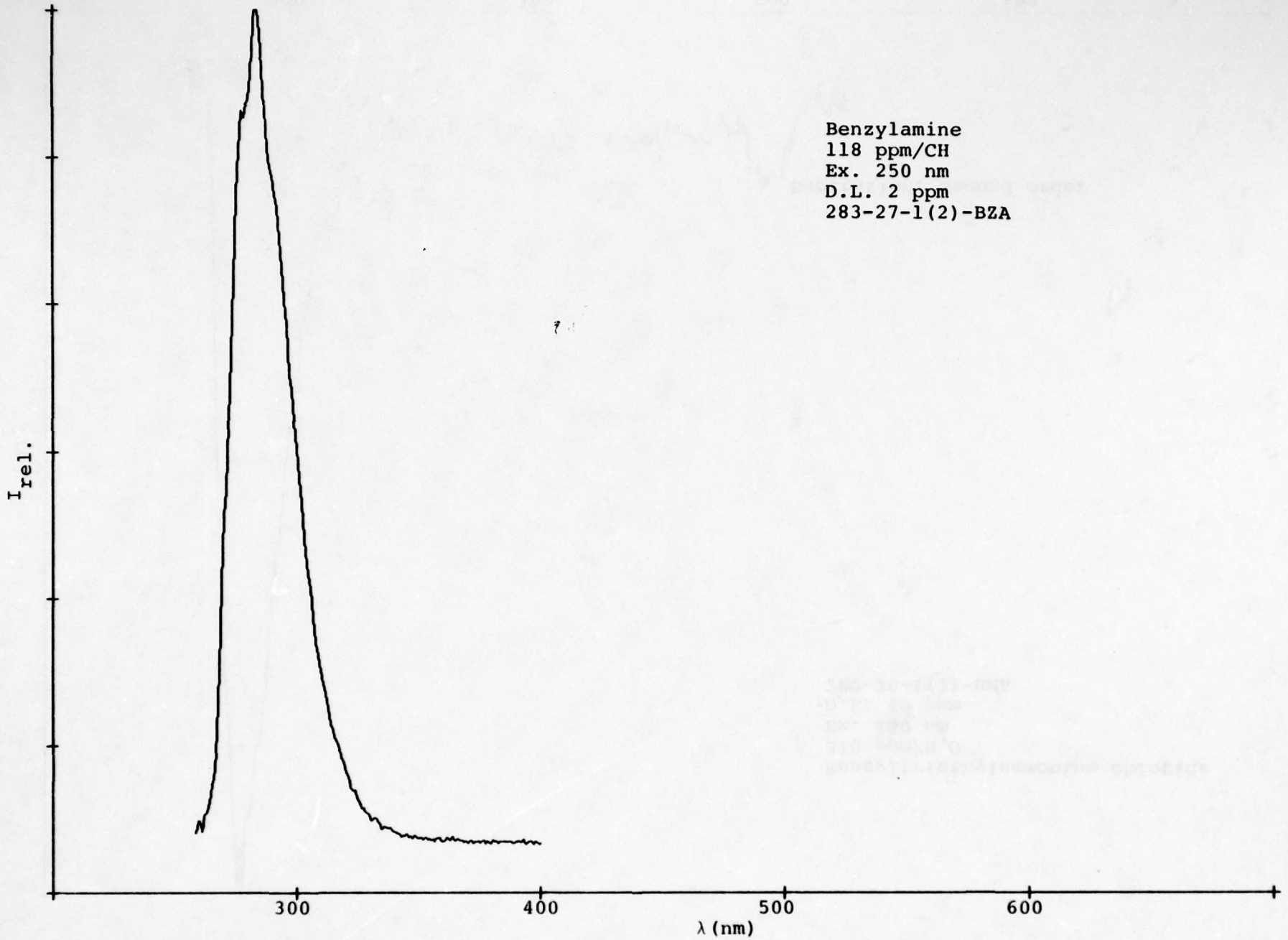

Benzo(a)pyrene
0.088 ppm/CH
Ex. 370 nm
D.L. 0.0002 ppm
405-5-6(2)-BAP
$I_{rel.}$
300
400
500
600
λ (nm)

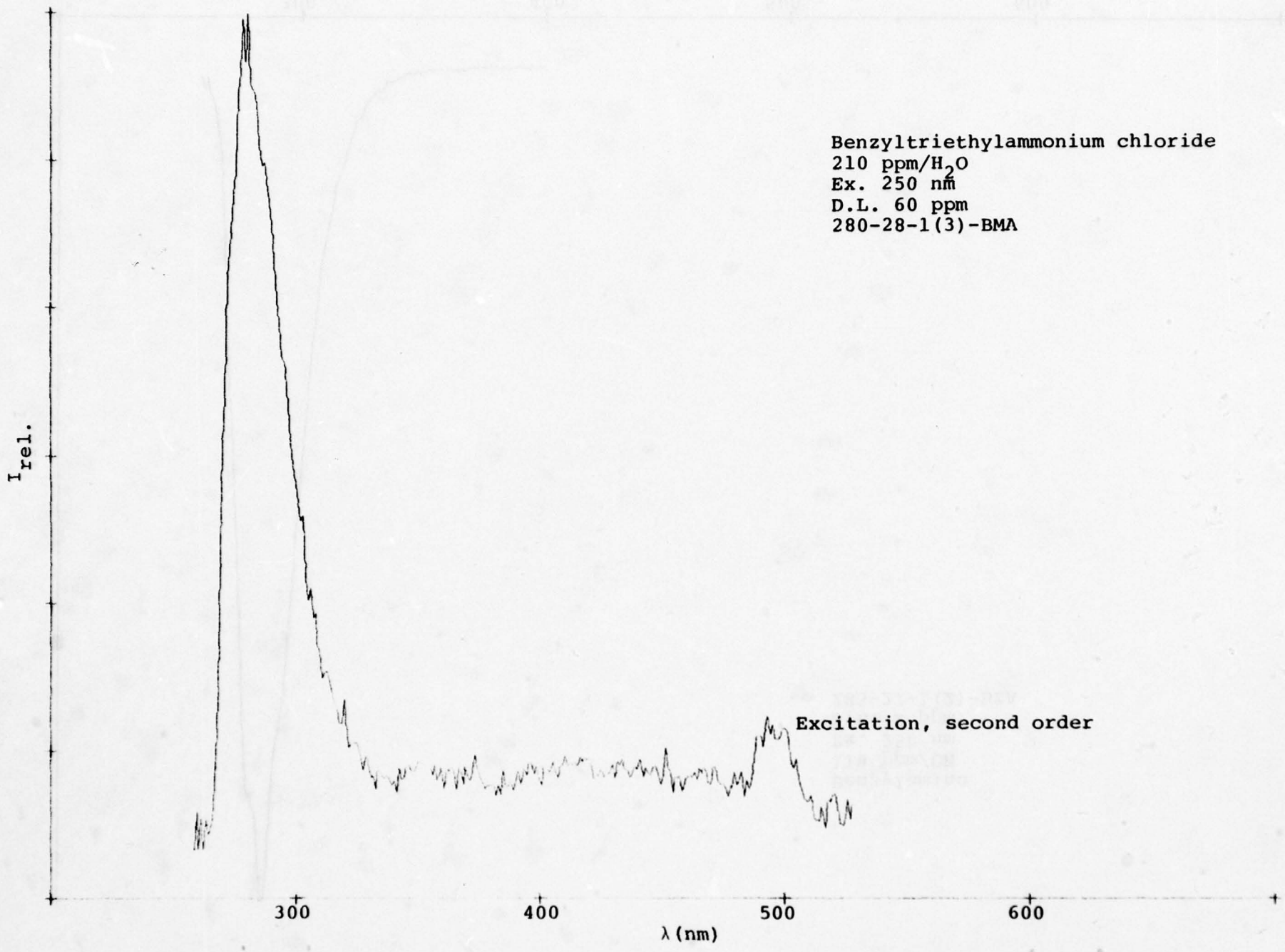

Benzoyl chloride
104 ppm/CH
Ex. 260 nm
Non-emitter
$I_{rel.}$
300
400
500
600
λ (nm)

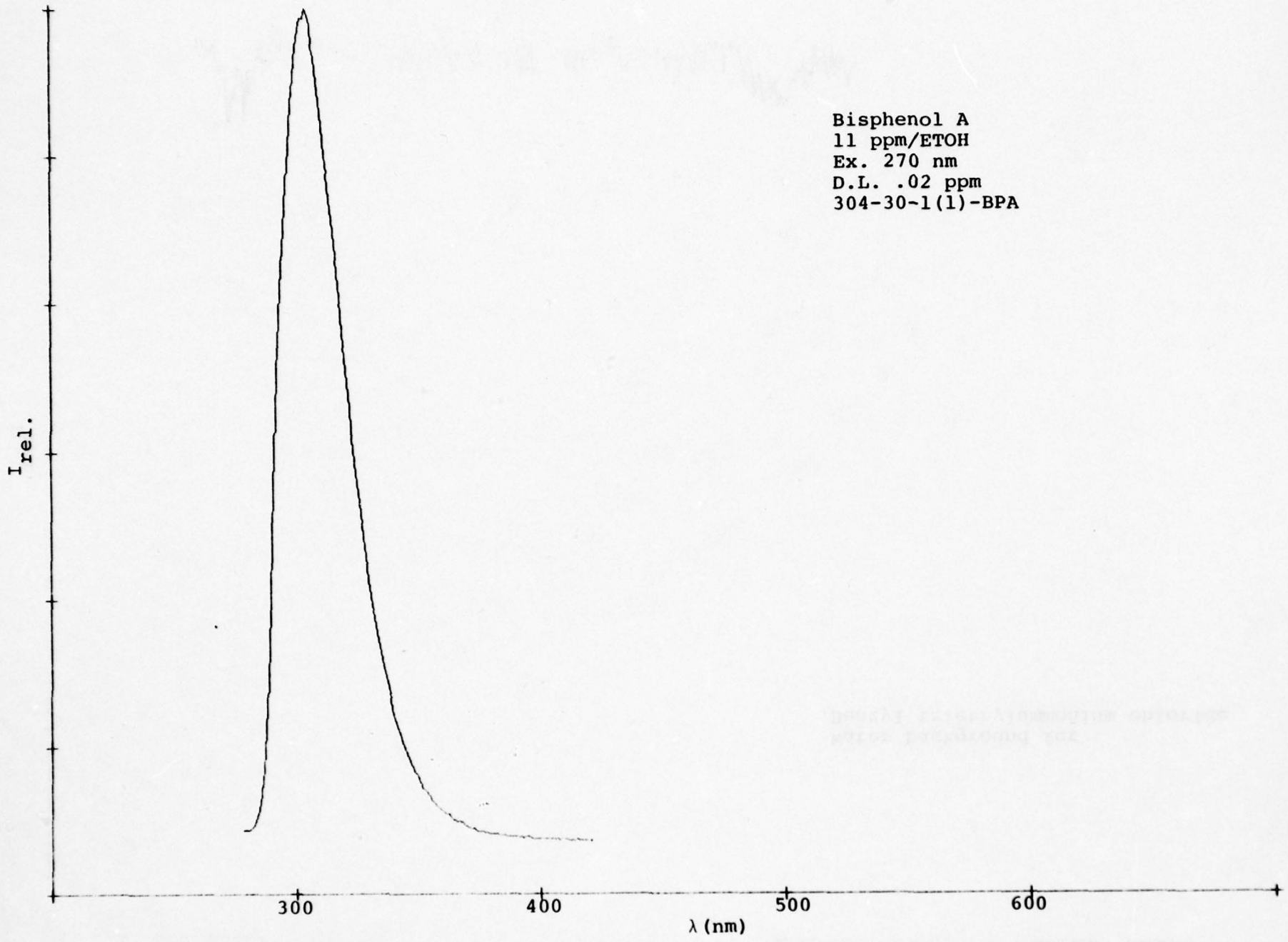


Cyclohexane background
for Benzoyl Chloride

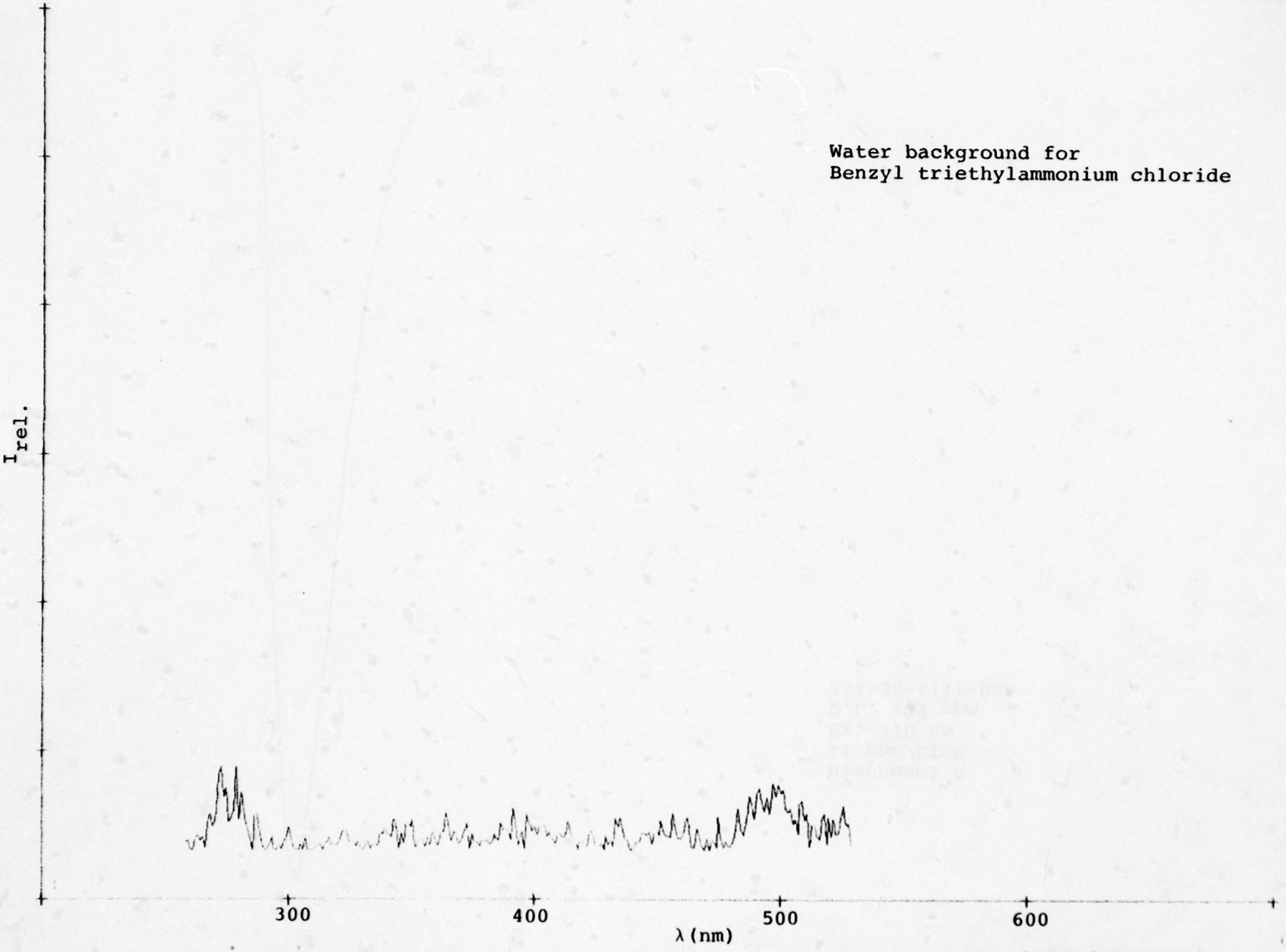

Benzyl alcohol
99 ppm/CH
Ex. 250 nm
D.L. 1 ppm
284-27-2(1)-BAL
$I_{rel.}$
300
400
500
600
λ (nm)

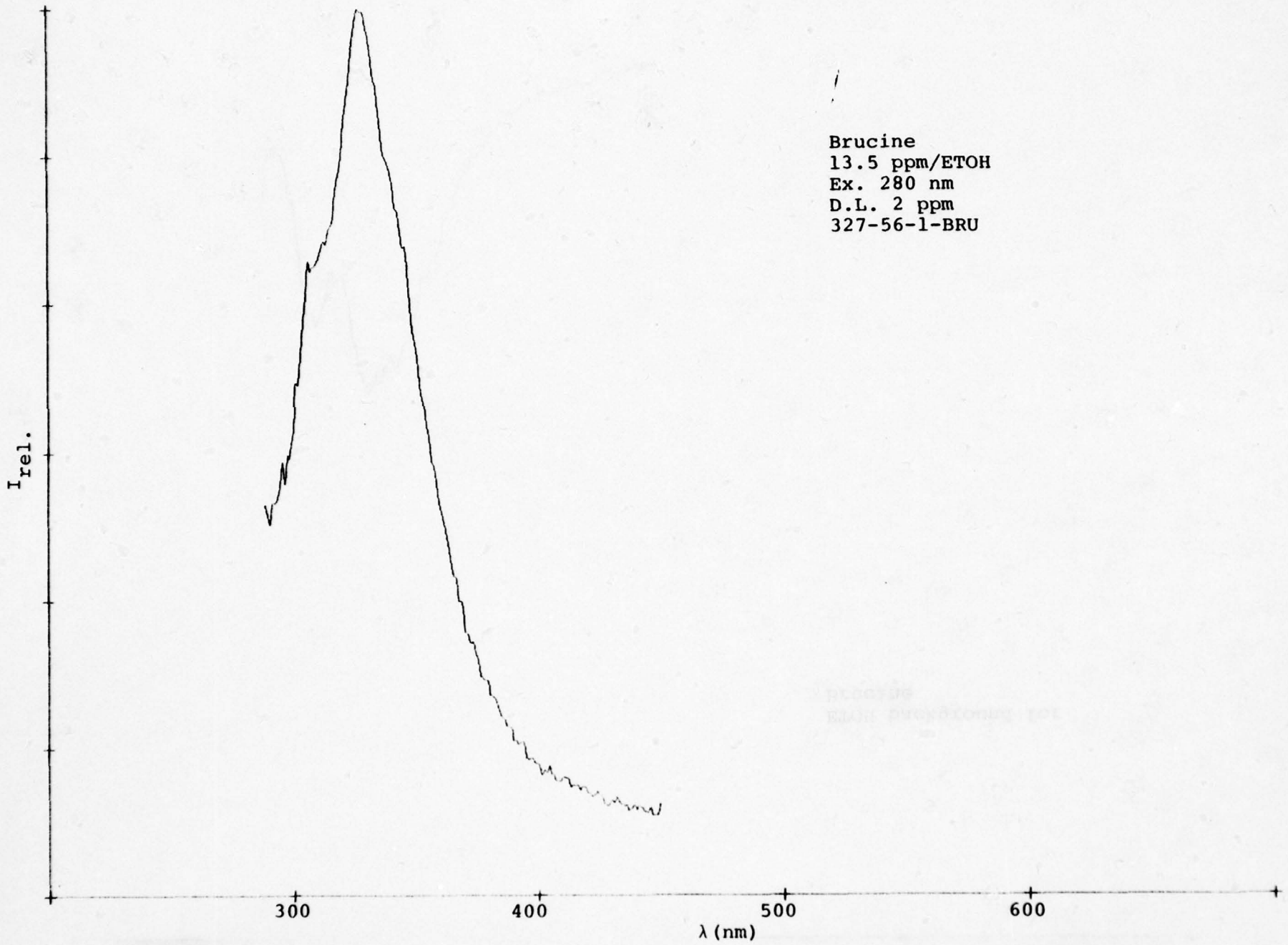

Benzylamine
118 ppm/CH
Ex. 250 nm
D.L. 2 ppm
283-27-1(2)-BZA
$I_{rel.}$
300
400
500
600
λ (nm)


Benzyltriethylammonium chloride
210 ppm/H_2O
Ex. 250 nm
D.L. 60 ppm
280-28-1(3)-BMA
$I_{rel.}$
Excitation, second order
300
400
500
600
λ (nm)

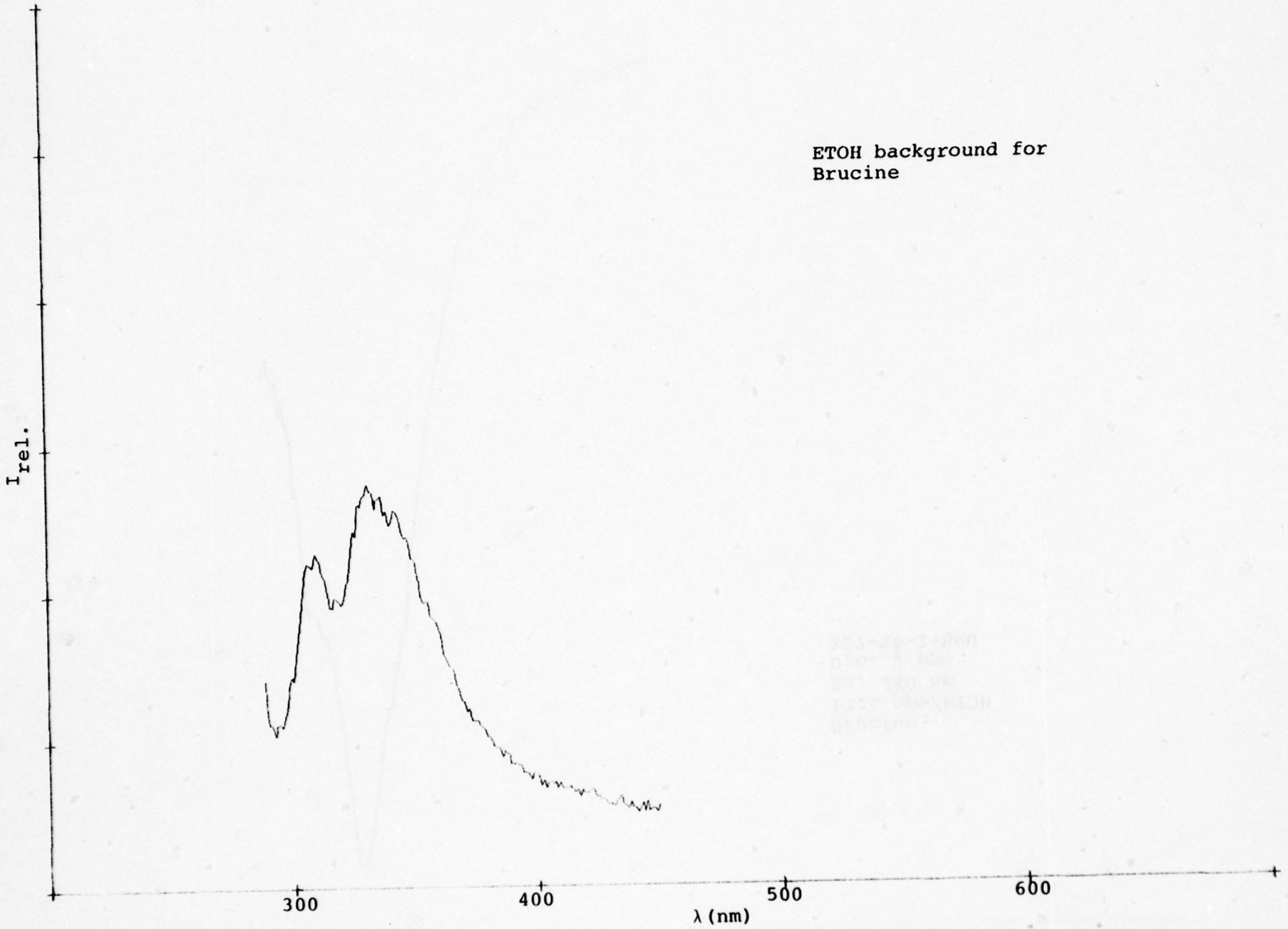

Bisphenol A
11 ppm/ETOH
Ex. 270 nm
D.L. .02 ppm
304-30-1(1)-BPA
$I_{rel.}$
300
400
500
600
λ (nm)

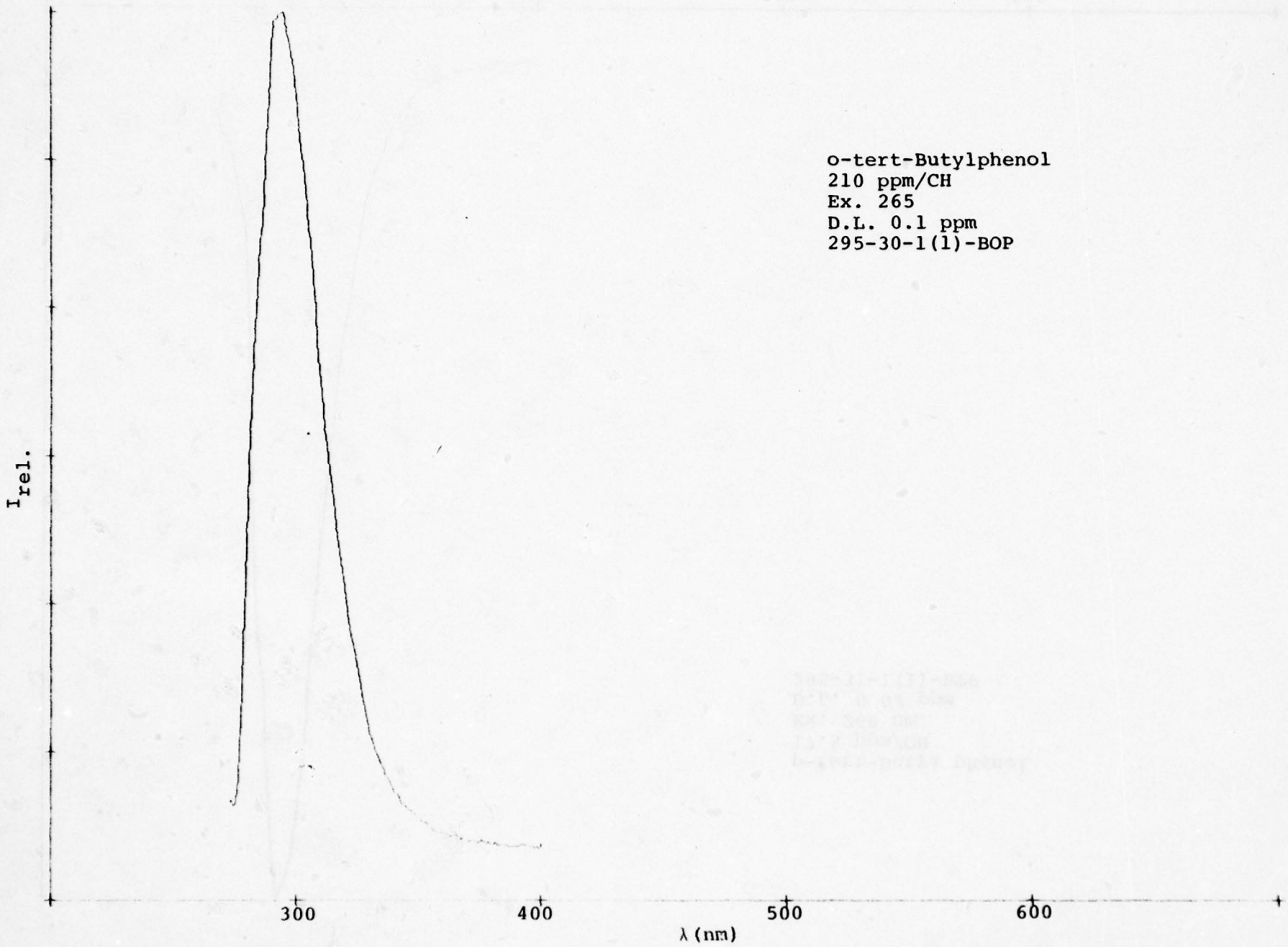
Water background for
Benzyl triethylammonium chloride



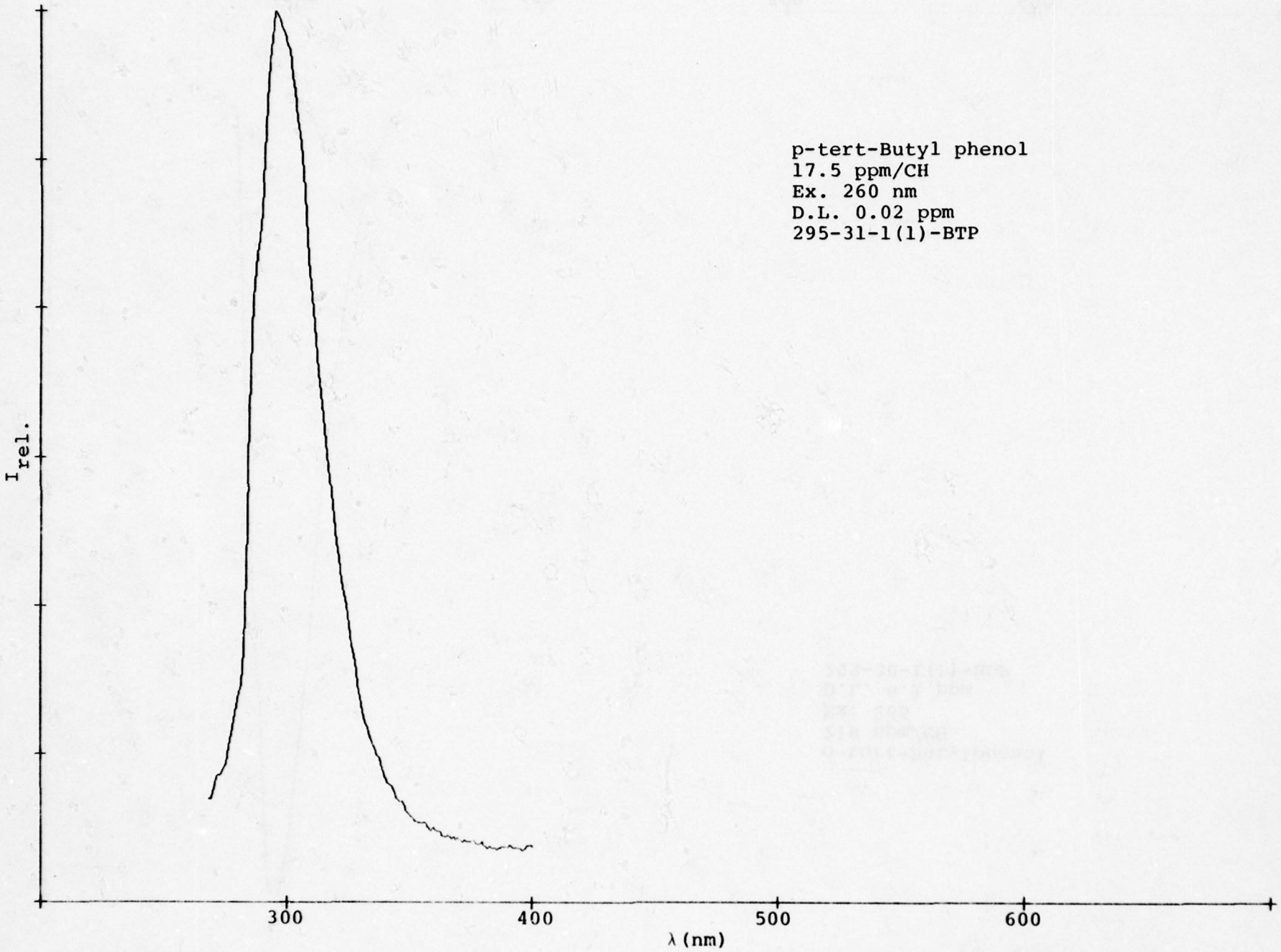

Brucine
13.5 ppm/ETOH
Ex. 280 nm
D.L. 2 ppm
327-56-1-BRU
Irel.
300
400
500
600
λ (nm)

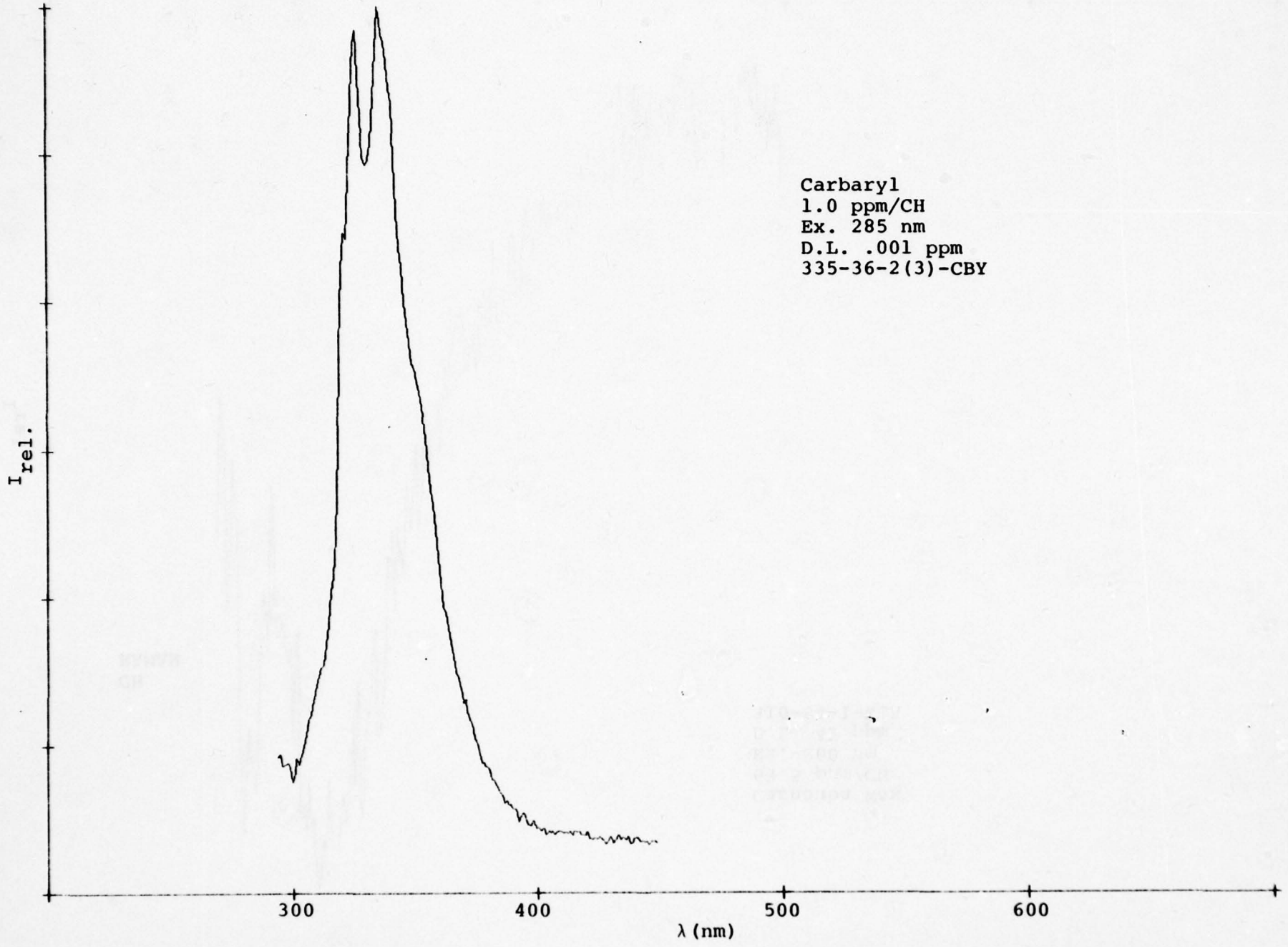
ETOH background for
Brucine

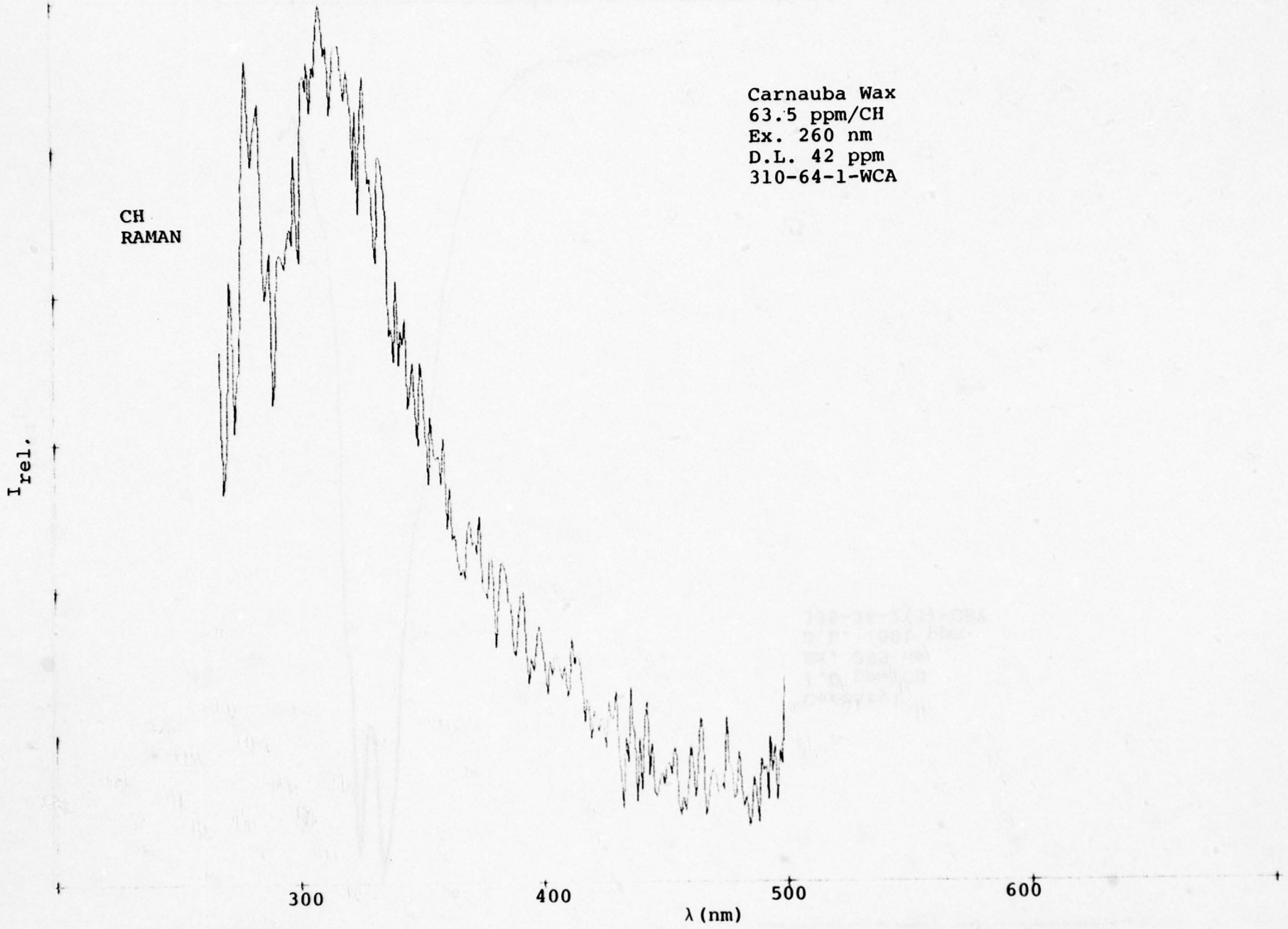


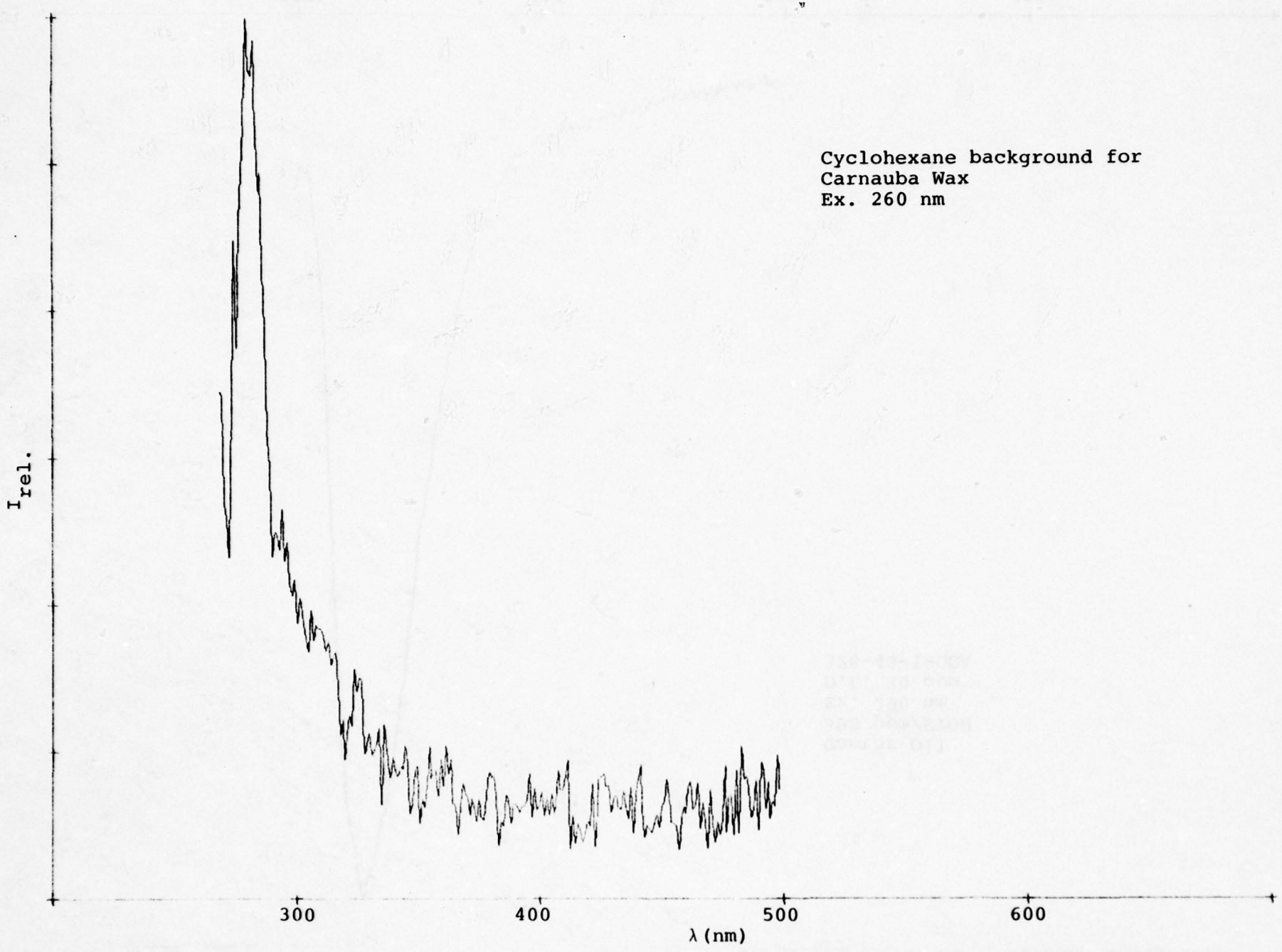


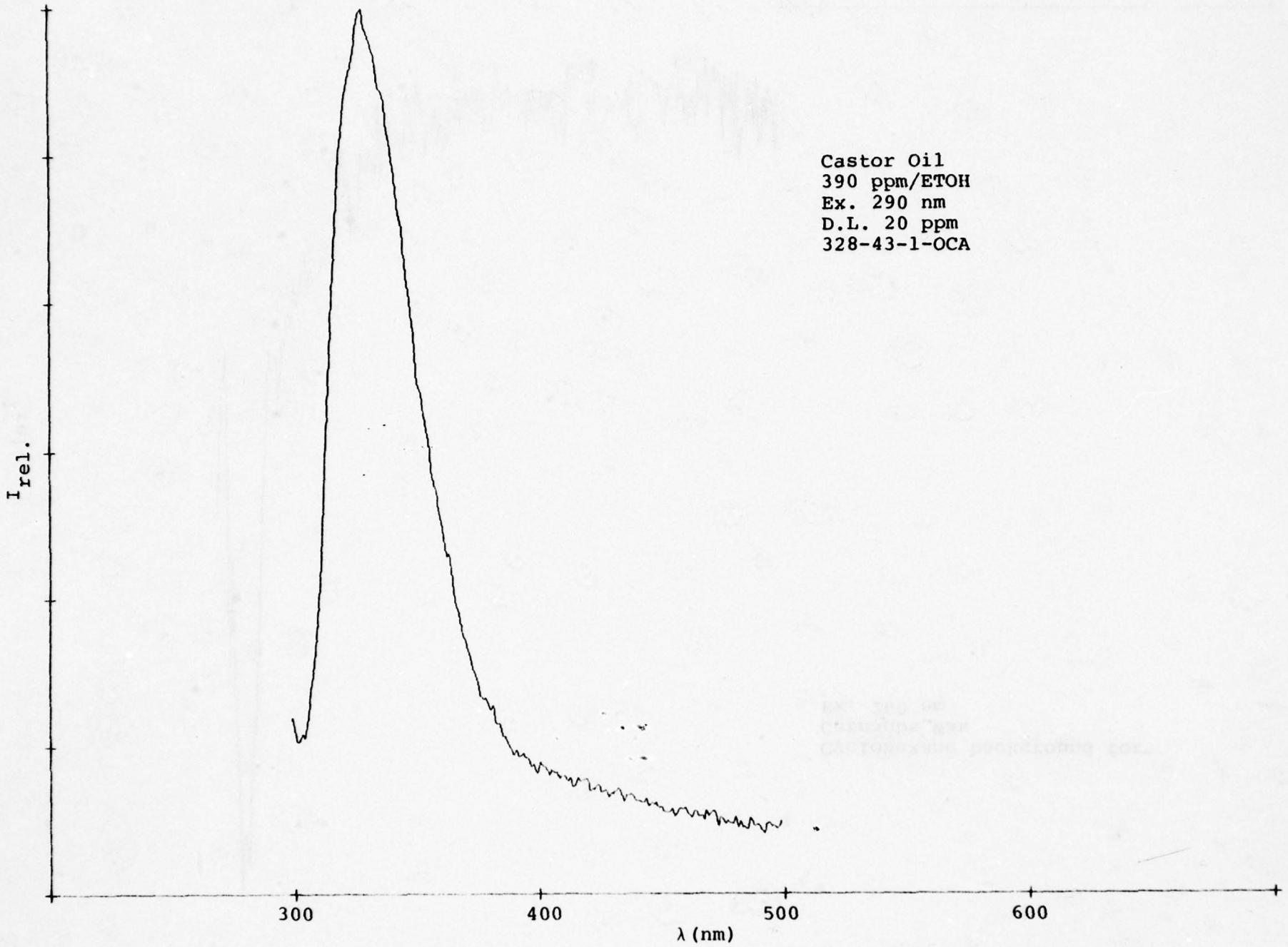
o-tert-Butylphenol
210 ppm/CH
Ex. 265
D.L. 0.1 ppm
295-30-1(1)-BOP


p-tert-Butyl phenol
17.5 ppm/CH
Ex. 260 nm
D.L. 0.02 ppm
295-31-1(1)-BTP
$I_{rel.}$
300
400
500
600
λ (nm)

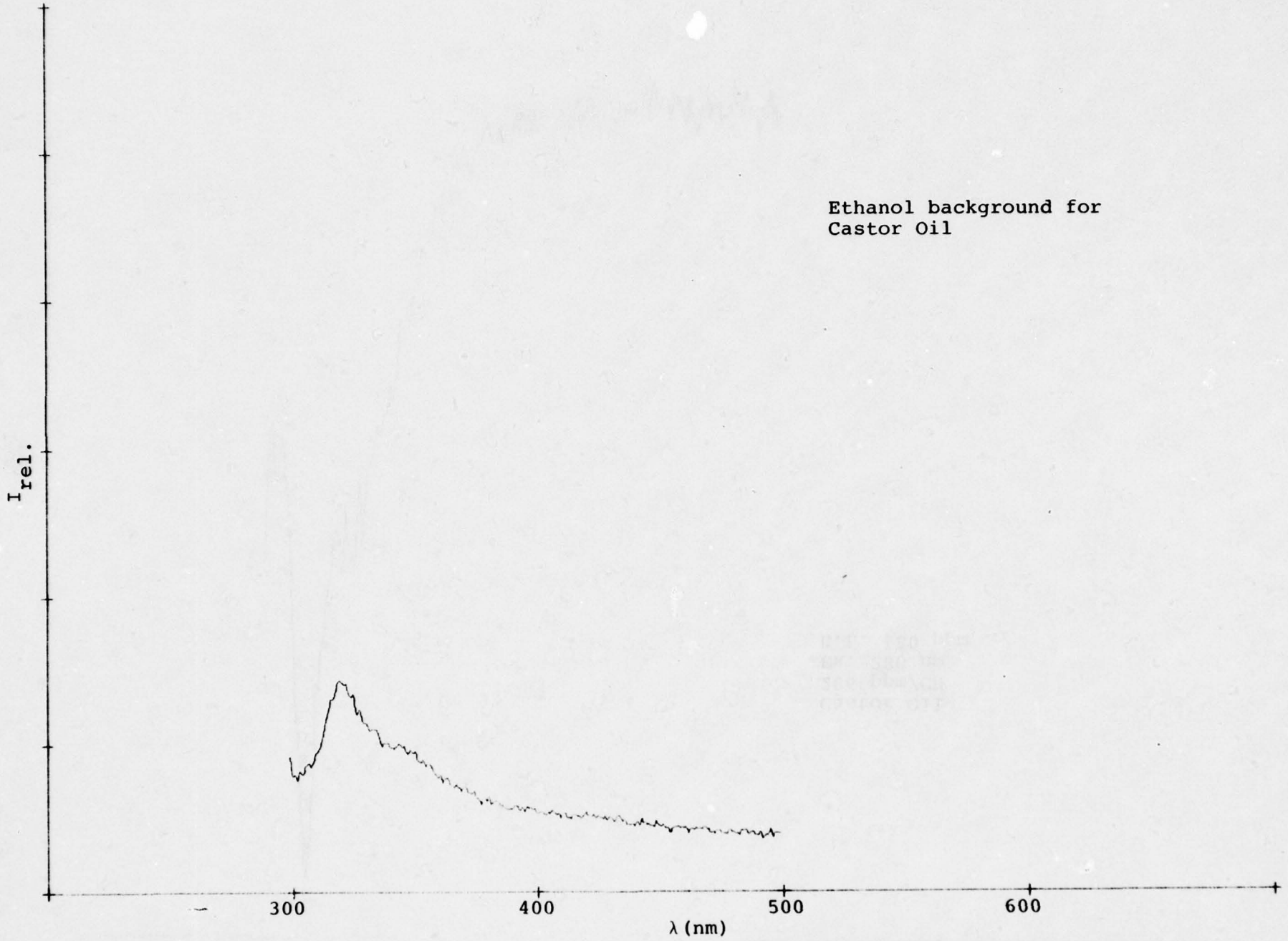

Carbaryl
1.0 ppm/CH
Ex. 285 nm
D.L. .001 ppm
335-36-2(3)-CBY
I rel.
300
400
500
600
λ (nm)

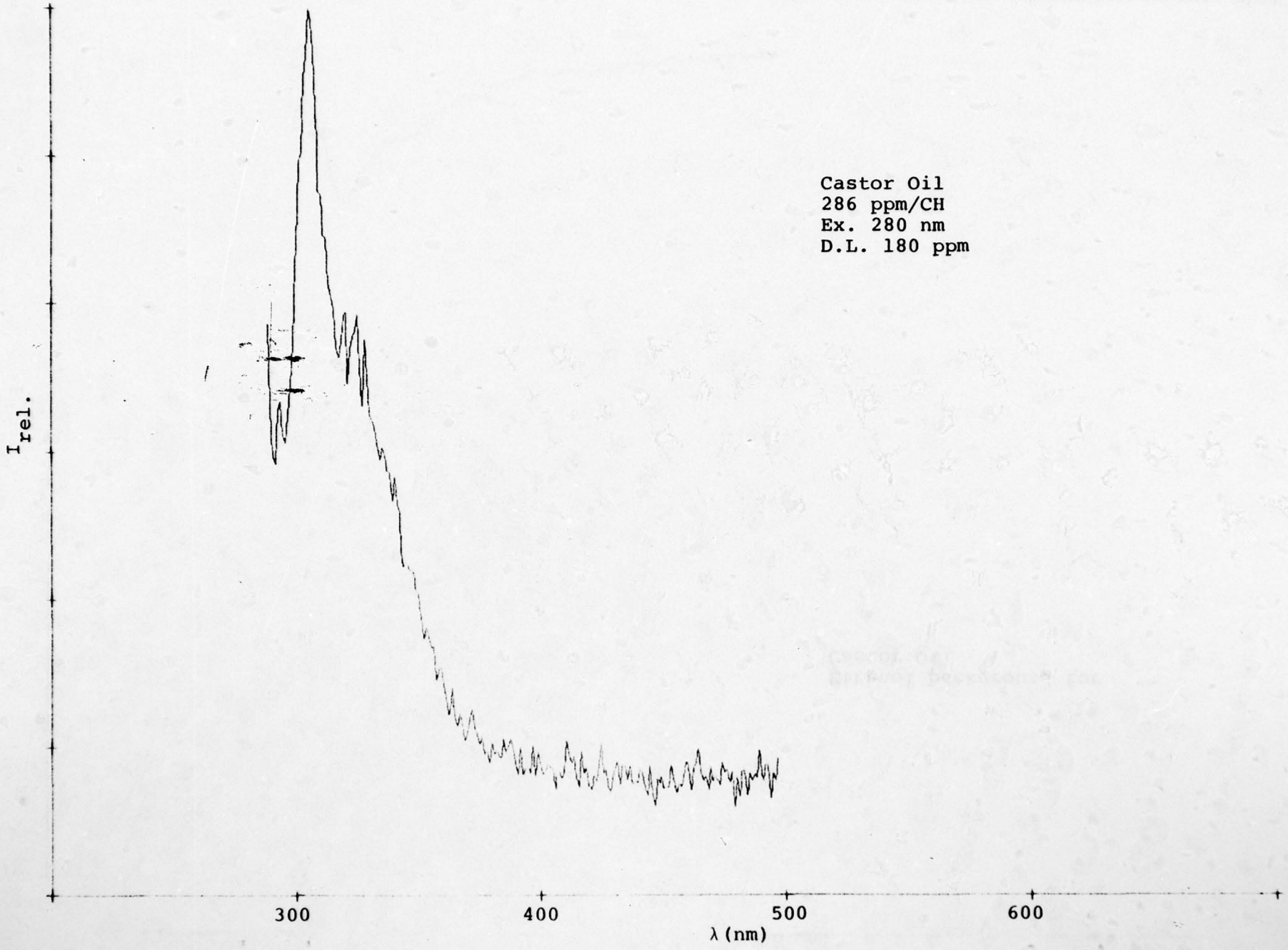

Carnauba Wax
63.5 ppm/CH
Ex. 260 nm
D.L. 42 ppm
310-64-1-WCA
CH
RAMAN
$I_{rel.}$
300
400
500
600
λ (nm)

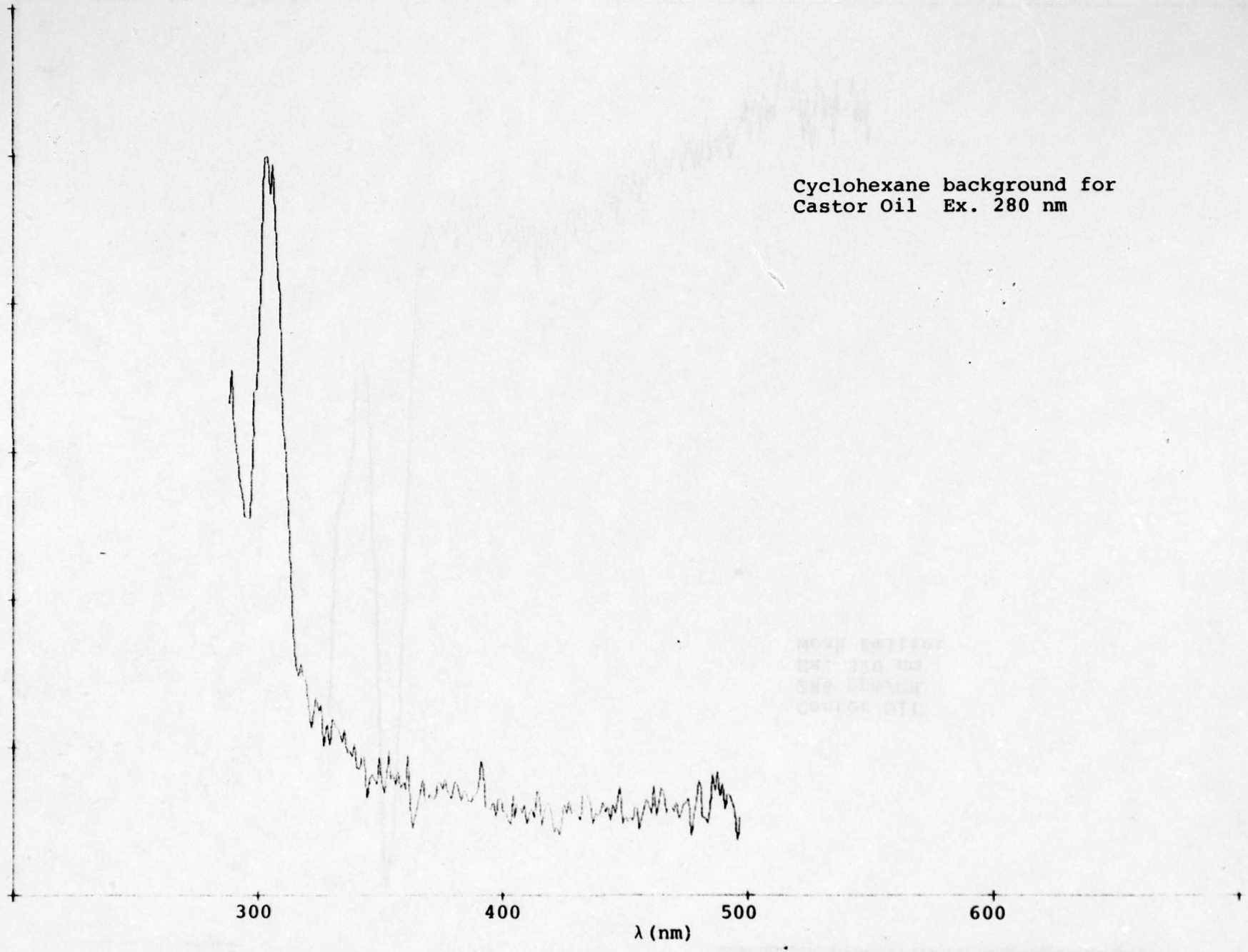

Cyclohexane background for
Carnauba Wax
Ex. 260 nm
$I_{rel.}$
300
400
500
600
λ (nm)

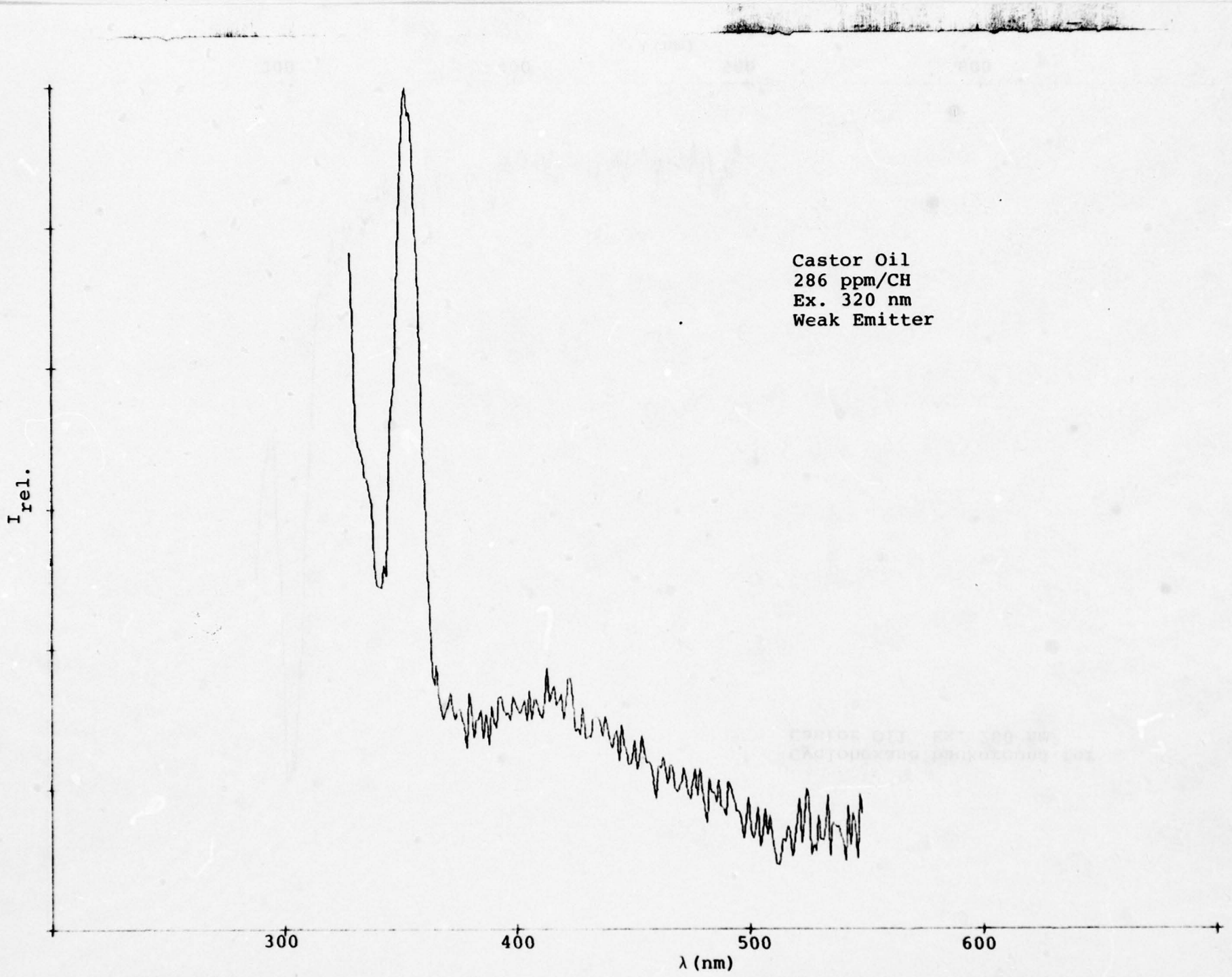

Castor Oil
390 ppm/ETOH
Ex. 290 nm
D.L. 20 ppm
328-43-1-OCA
I rel.
300
400
500
600
λ (nm)

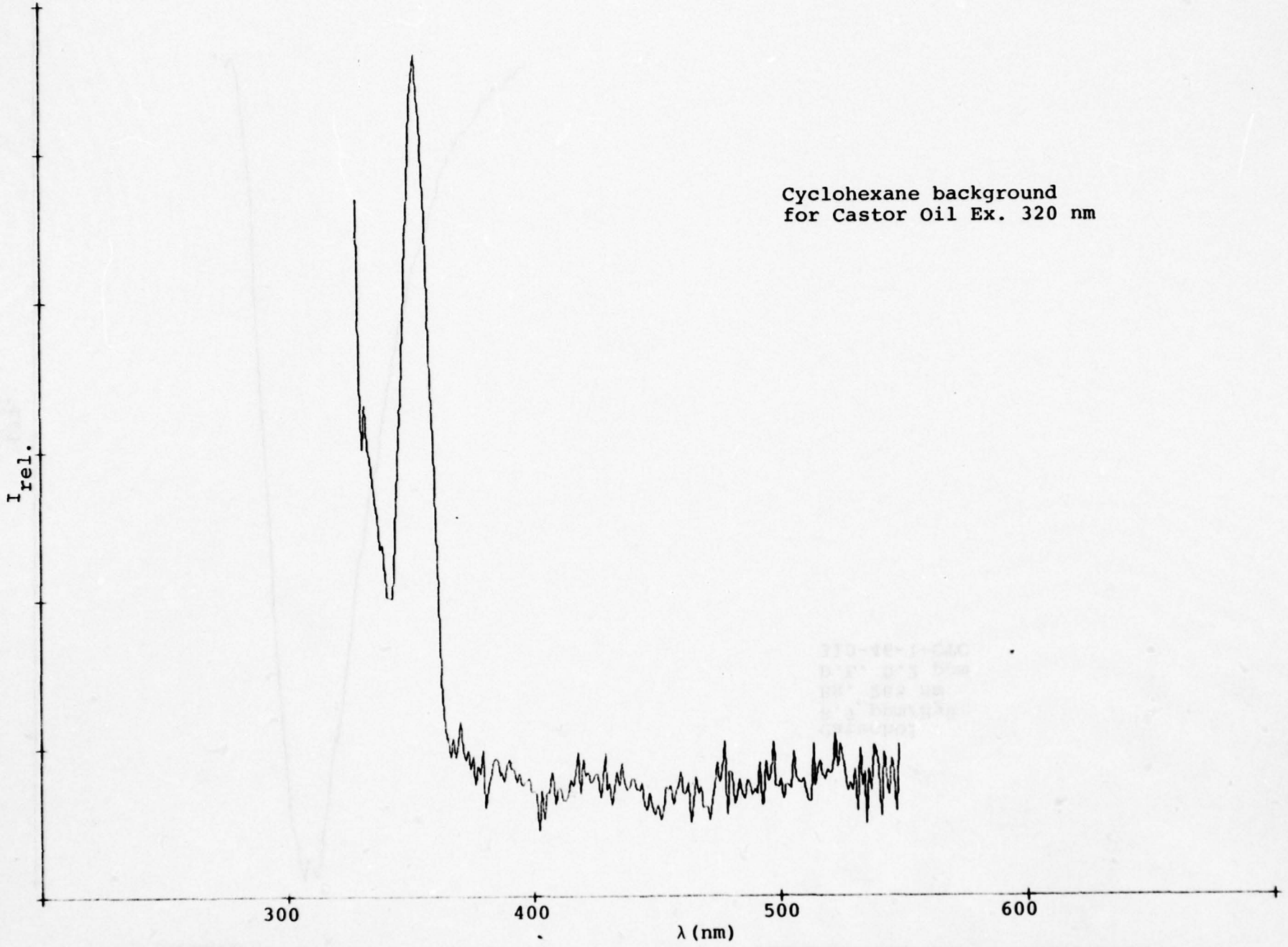
Ethanol background for
Castor Oil

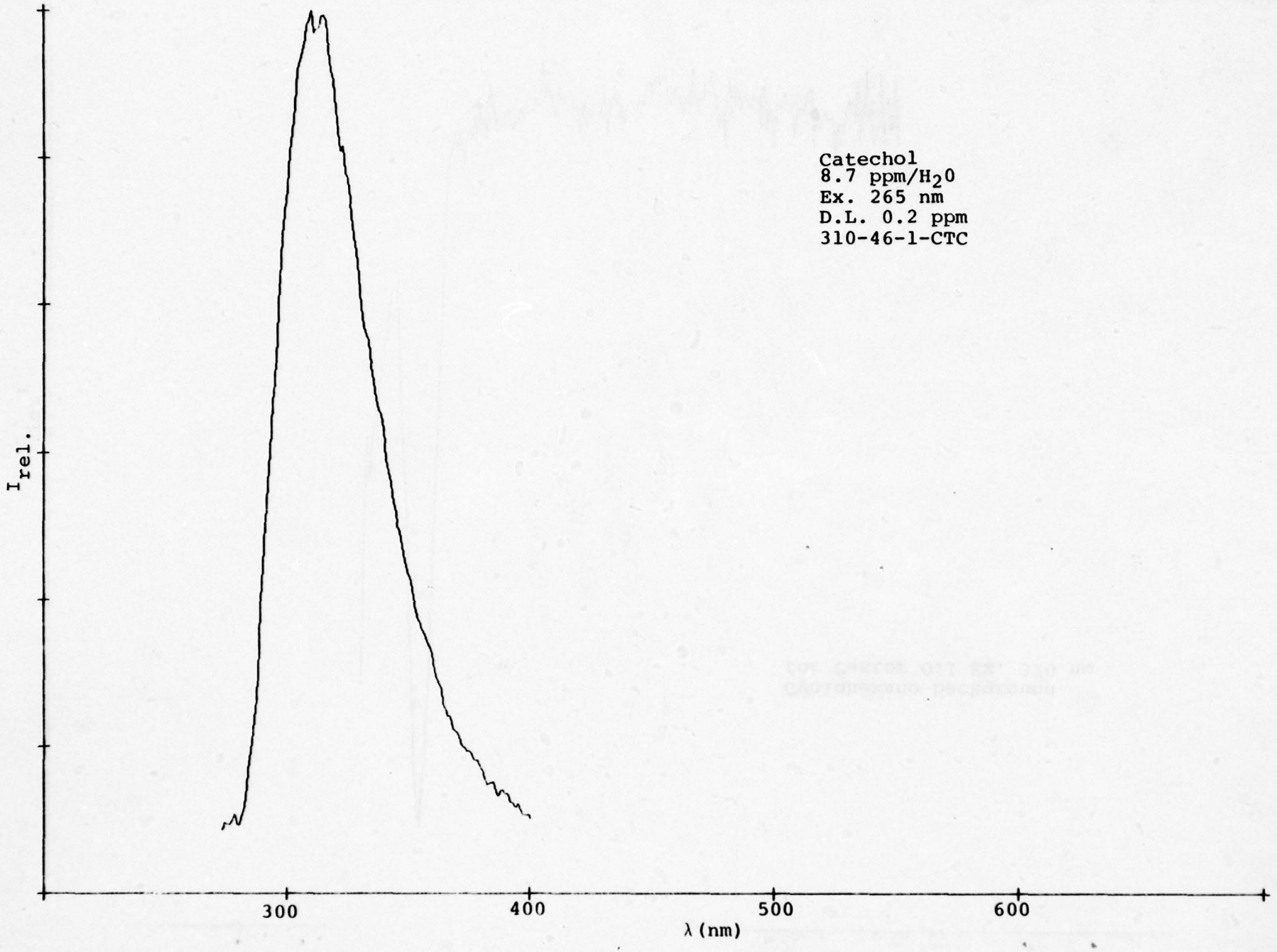


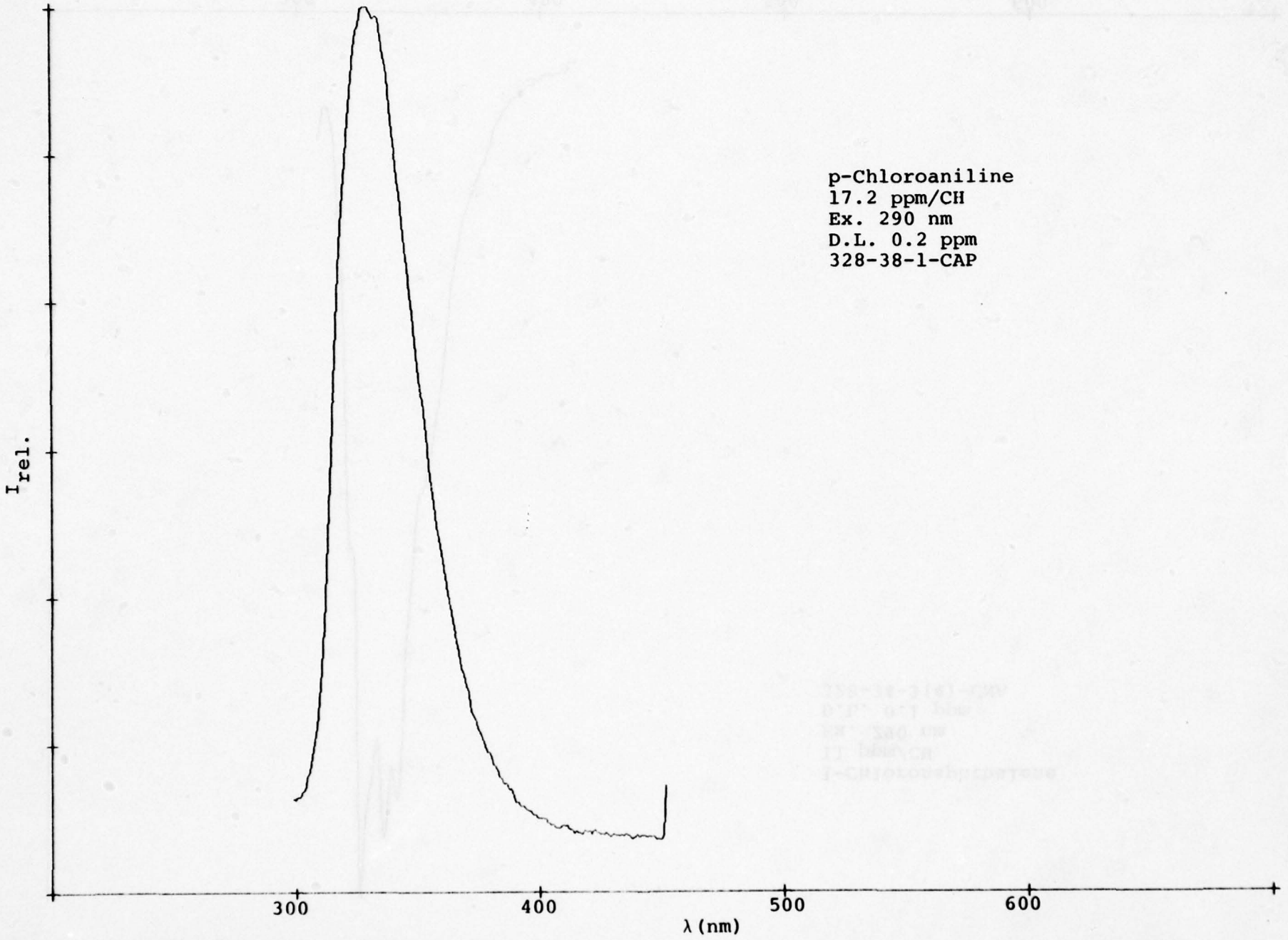

Castor Oil
286 ppm/CH
Ex. 280 nm
D.L. 180 ppm
$I_{rel.}$
300
400
500
600
λ (nm)

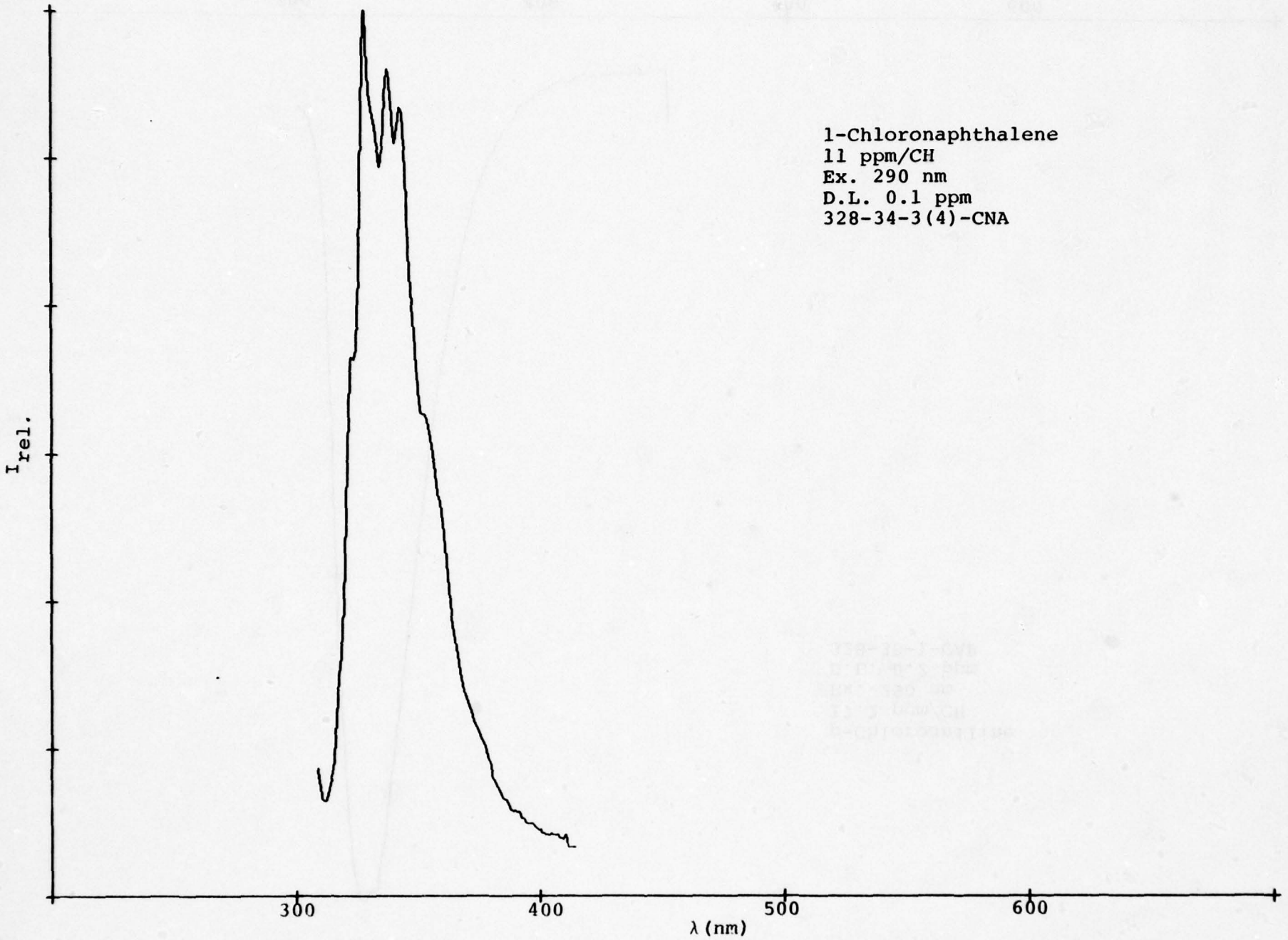

Cyclohexane background for
Castor Oil Ex. 280 nm
300
400
500
600
λ (nm)

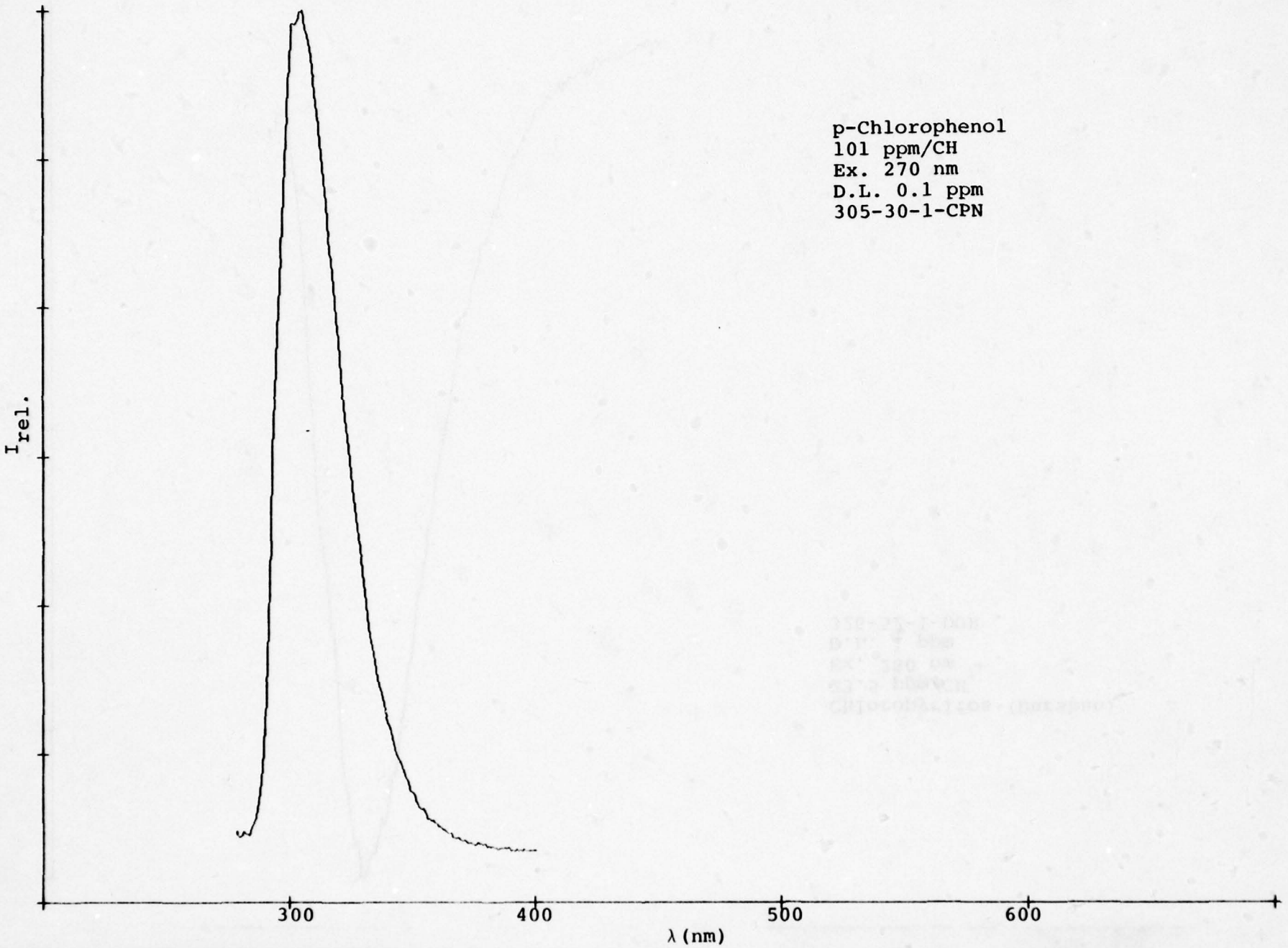

Castor Oil
286 ppm/CH
Ex. 320 nm
Weak Emitter
$I_{rel.}$
300
400
500
600
λ (nm)

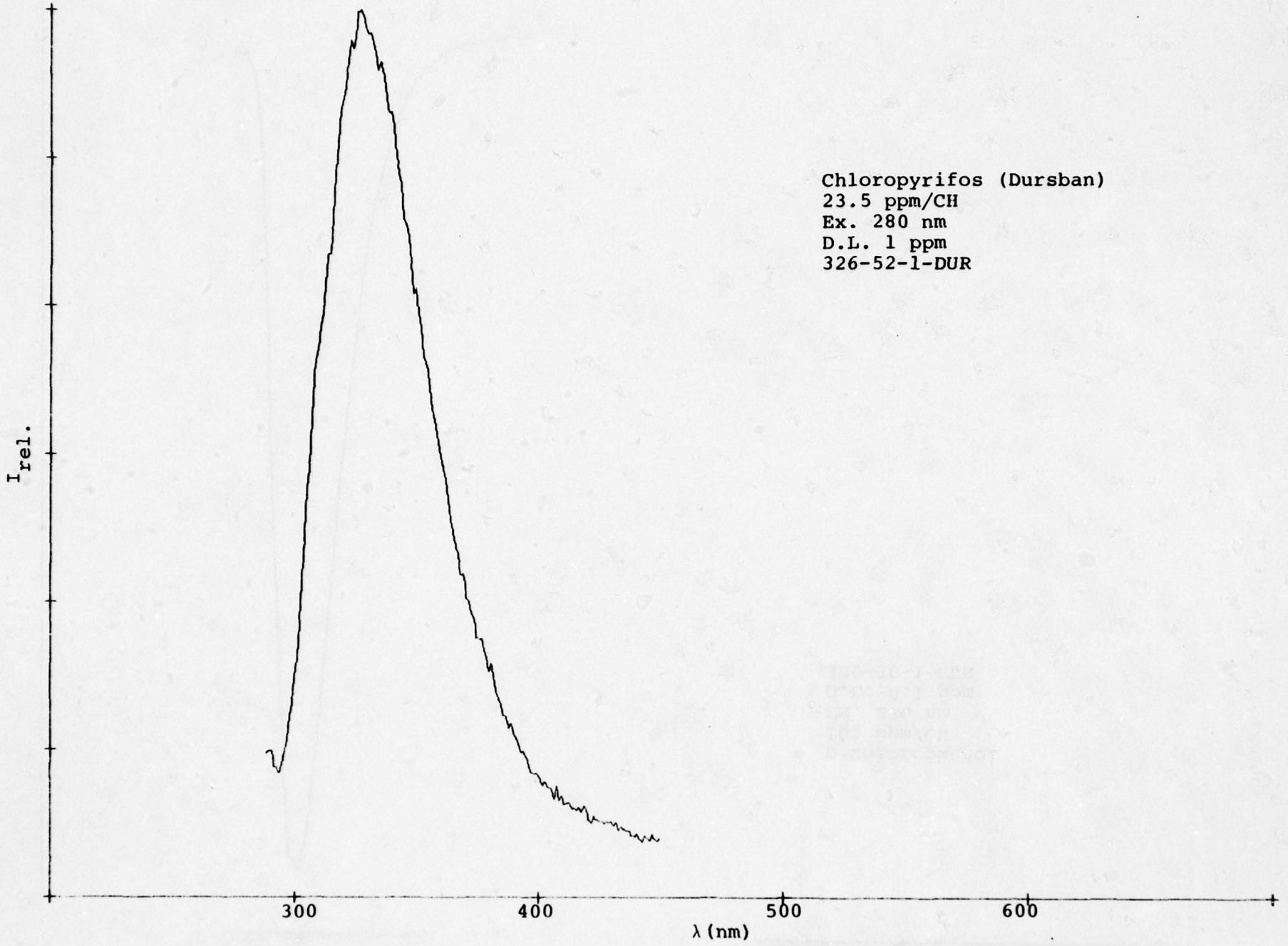

Cyclohexane background
for Castor Oil Ex. 320 nm
I rel.
300
400
500
600
λ (nm)

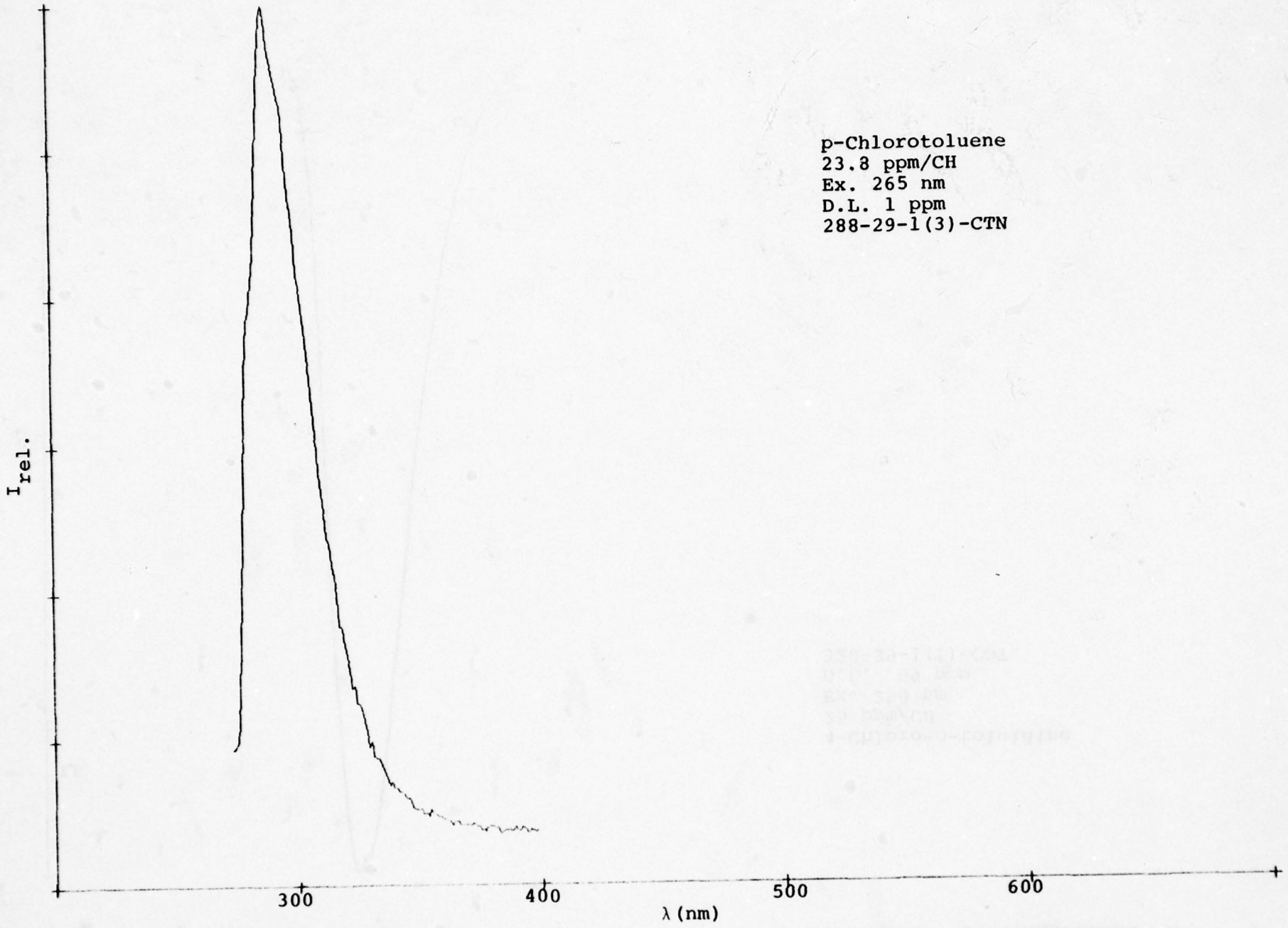

Catechol
8.7 ppm/H_2O
Ex. 265 nm
D.L. 0.2 ppm
310-46-1-CTC
$I_{rel.}$
300
400
500
600
λ (nm)

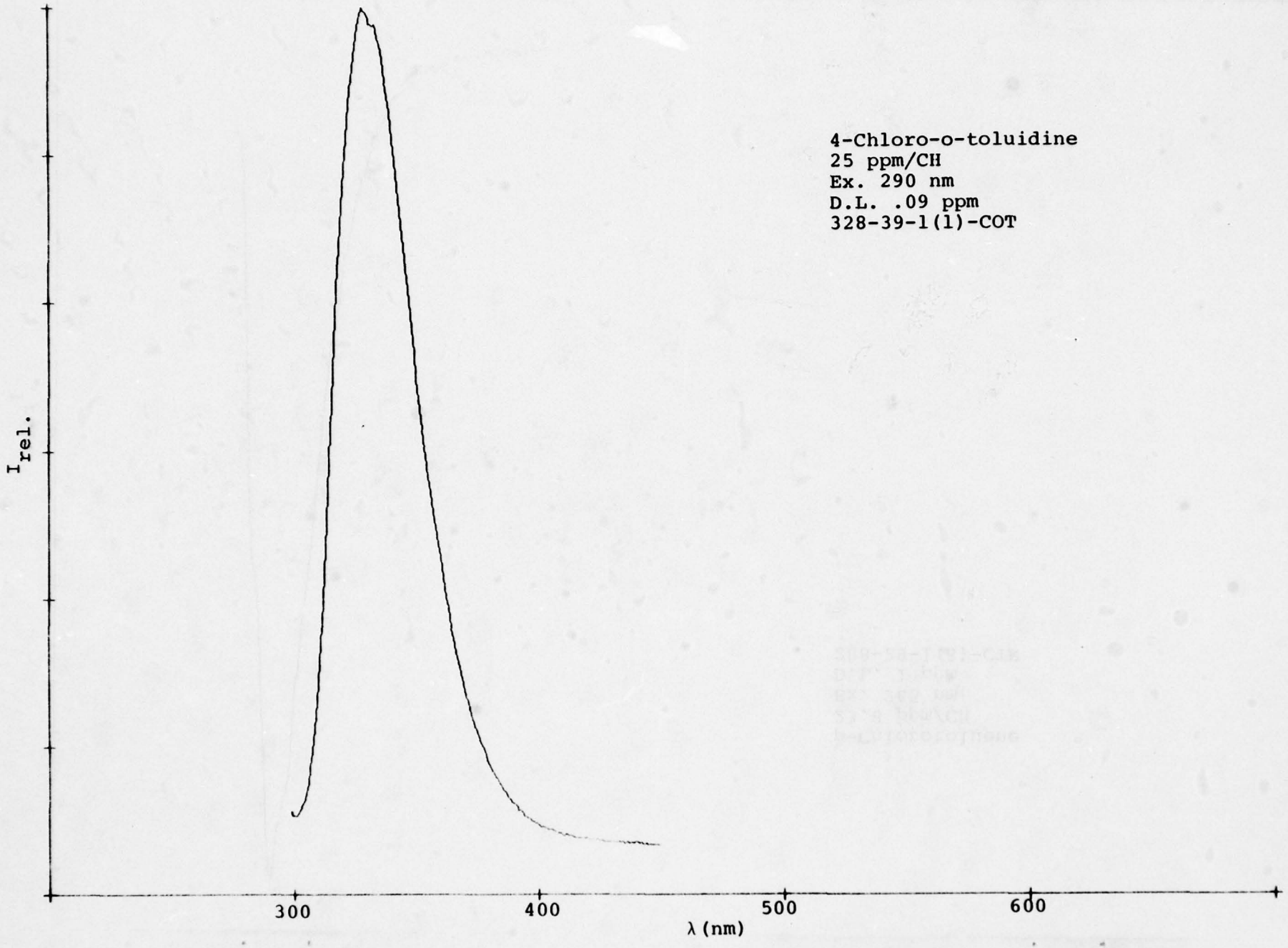

p-Chloroaniline
17.2 ppm/CH
Ex. 290 nm
D.L. 0.2 ppm
328-38-1-CAP
I rel.
300
400
500
600
λ (nm)

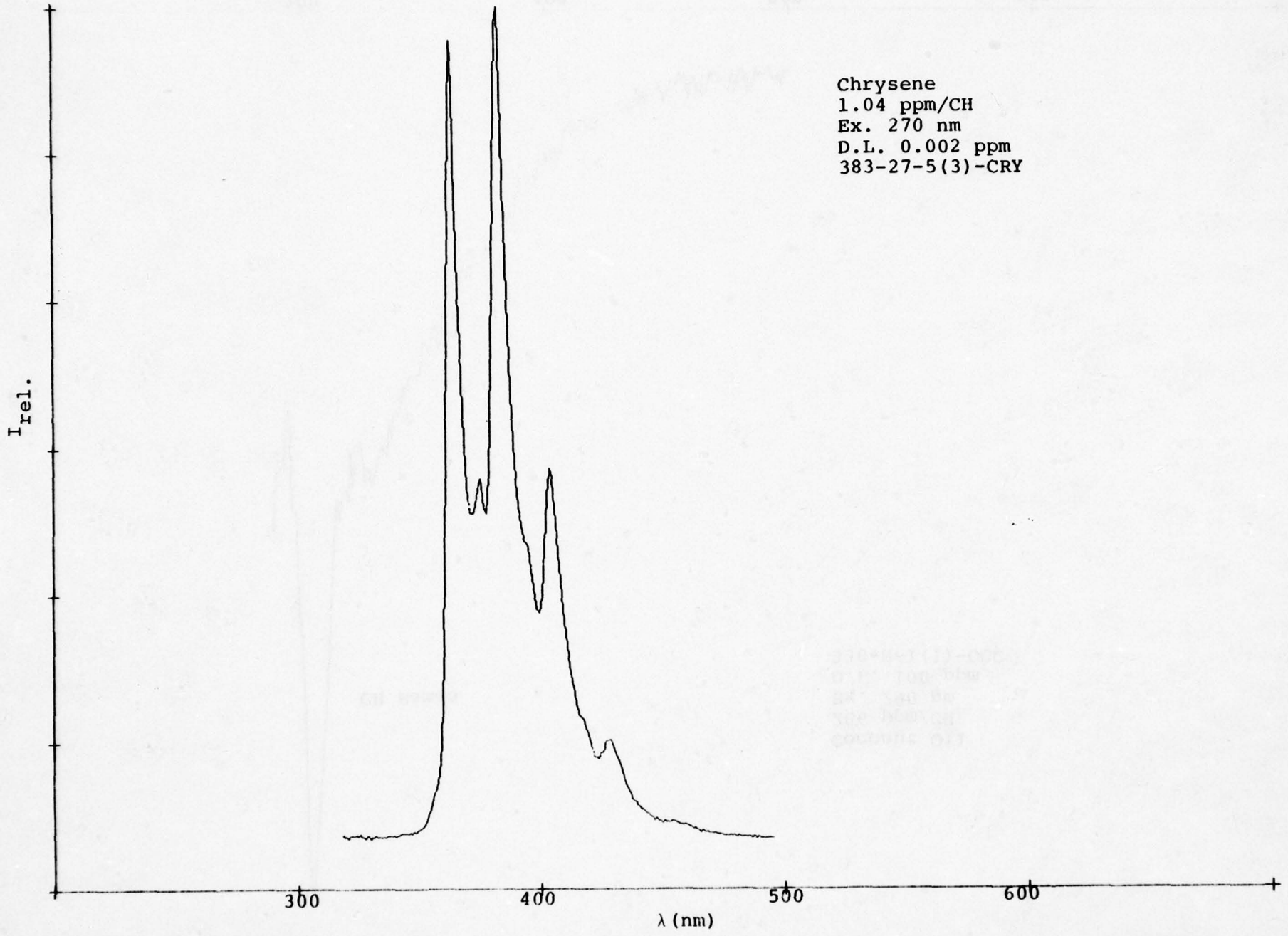

1-Chloronaphthalene
11 ppm/CH
Ex. 290 nm
D.L. 0.1 ppm
328-34-3(4)-CNA
$I_{rel.}$
300
400
500
600
λ (nm)

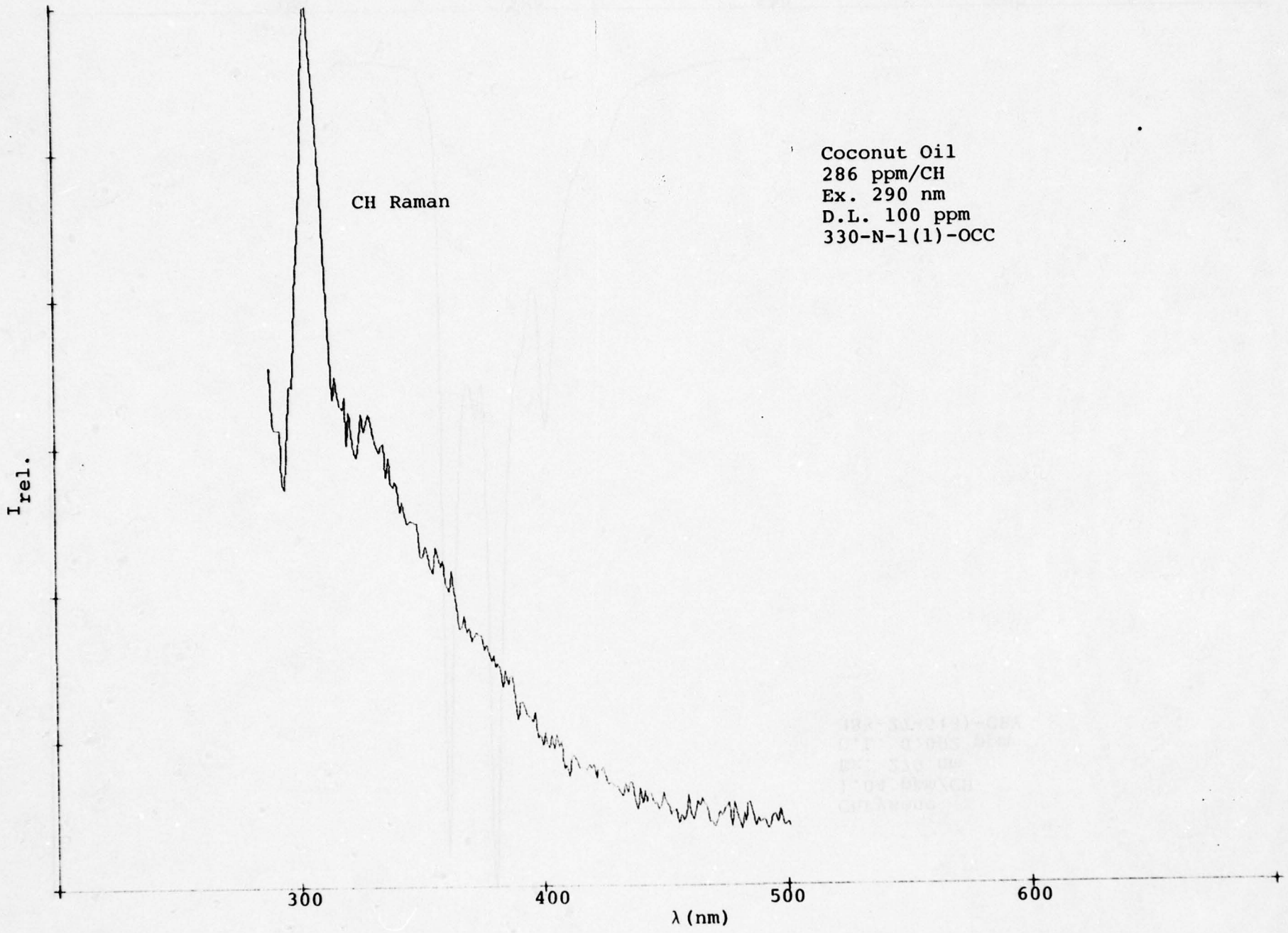

p-Chlorophenol
101 ppm/CH
Ex. 270 nm
D.L. 0.1 ppm
305-30-1-CPN
I rel.
300
400
500
600
λ (nm)


Chloropyrifos (Dursban)
23.5 ppm/CH
Ex. 280 nm
D.L. 1 ppm
326-52-1-DUR
$I_{rel.}$
300
400
500
600
λ (nm)

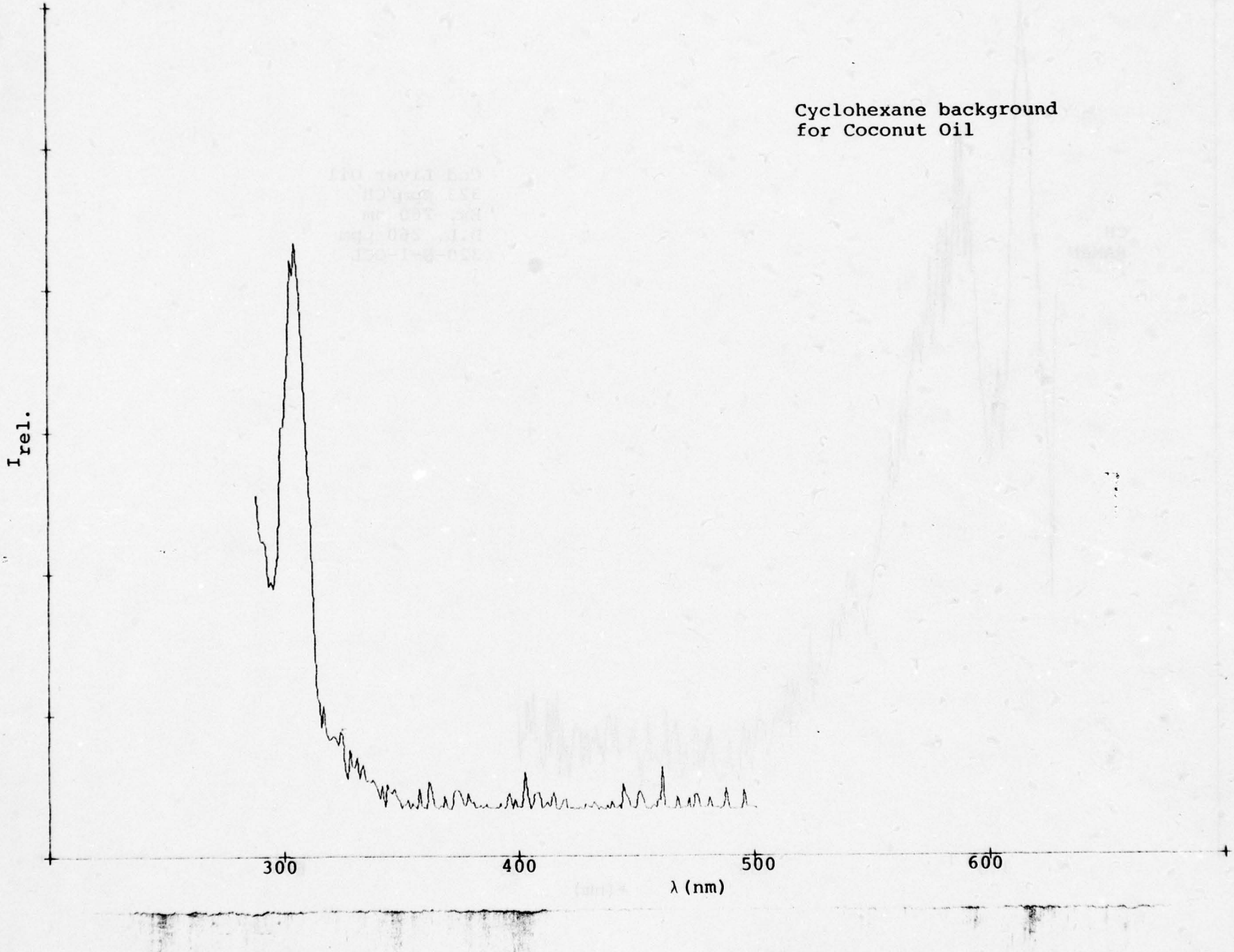

p-Chlorotoluene
23.8 ppm/CH
Ex. 265 nm
D.L. 1 ppm
288-29-1(3)-CTN
$I_{rel.}$
300
400
500
600
λ (nm)

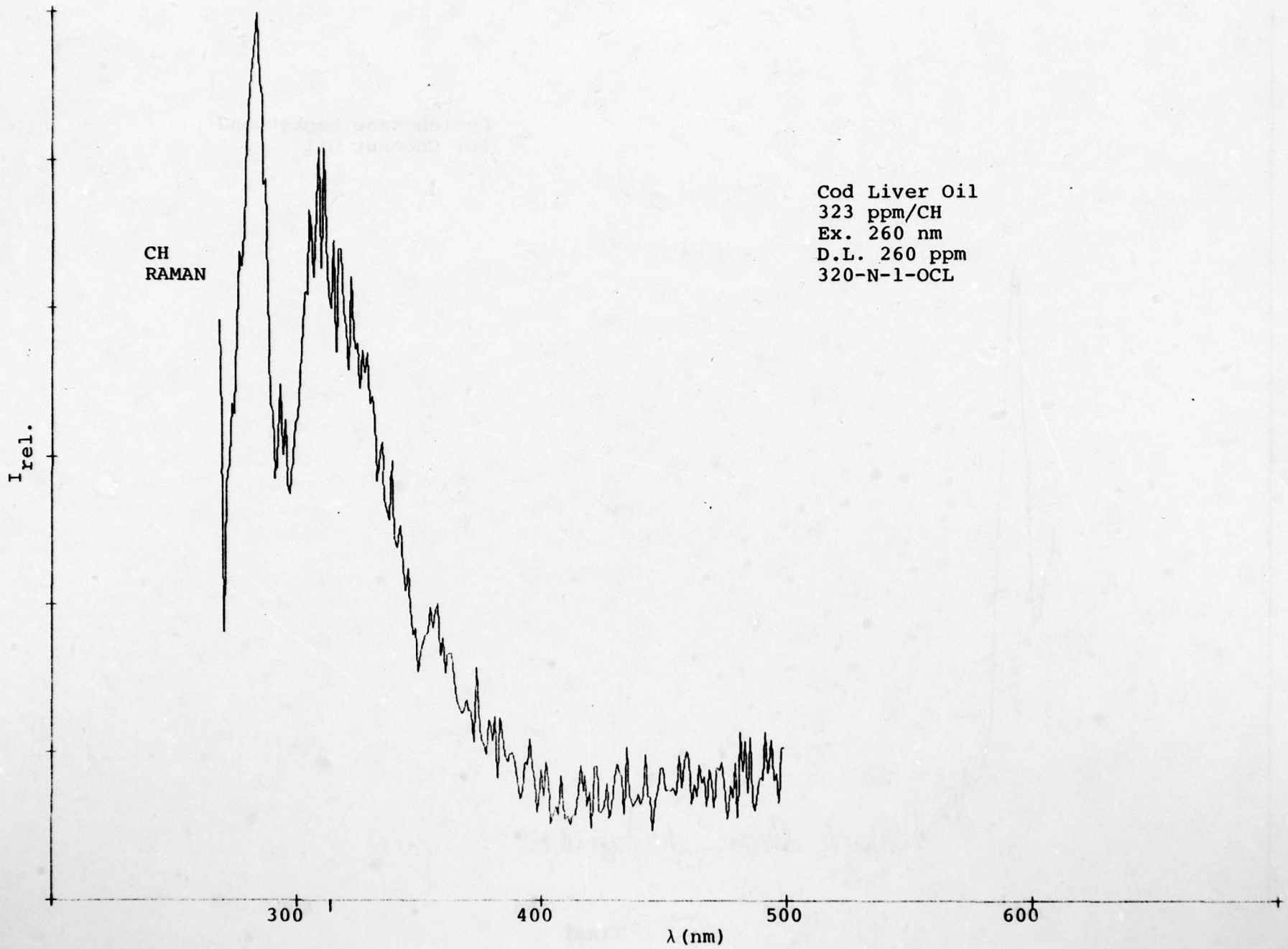

4-Chloro-o-toluidine
25 ppm/CH
Ex. 290 nm
D.L. .09 ppm
328-39-1(1)-COT
I rel.
300
400
500
600
λ (nm)

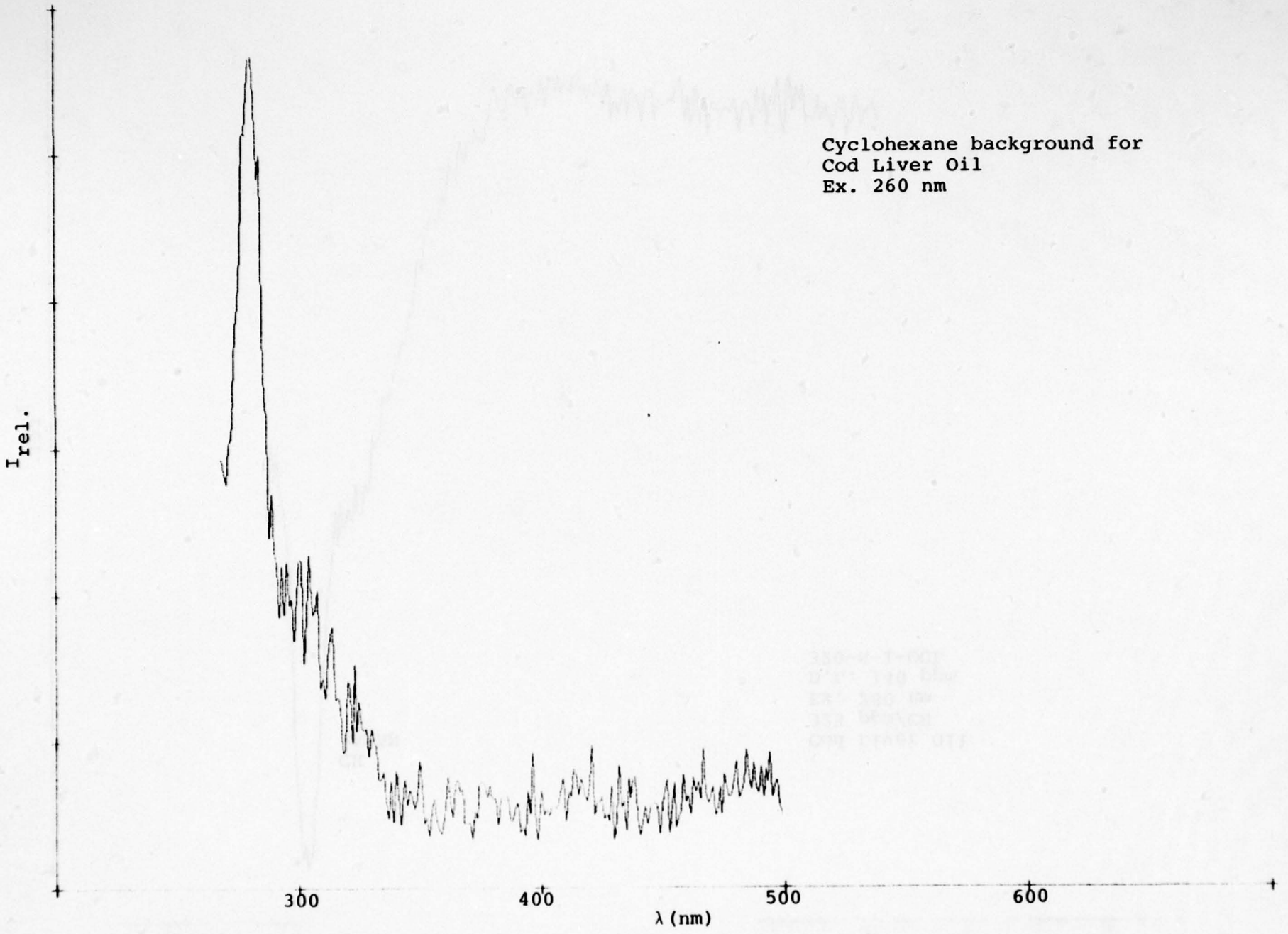

Chrysene
1.04 ppm/CH
Ex. 270 nm
D.L. 0.002 ppm
383-27-5(3)-CRY
$I_{rel.}$
300
400
500
600
λ (nm)

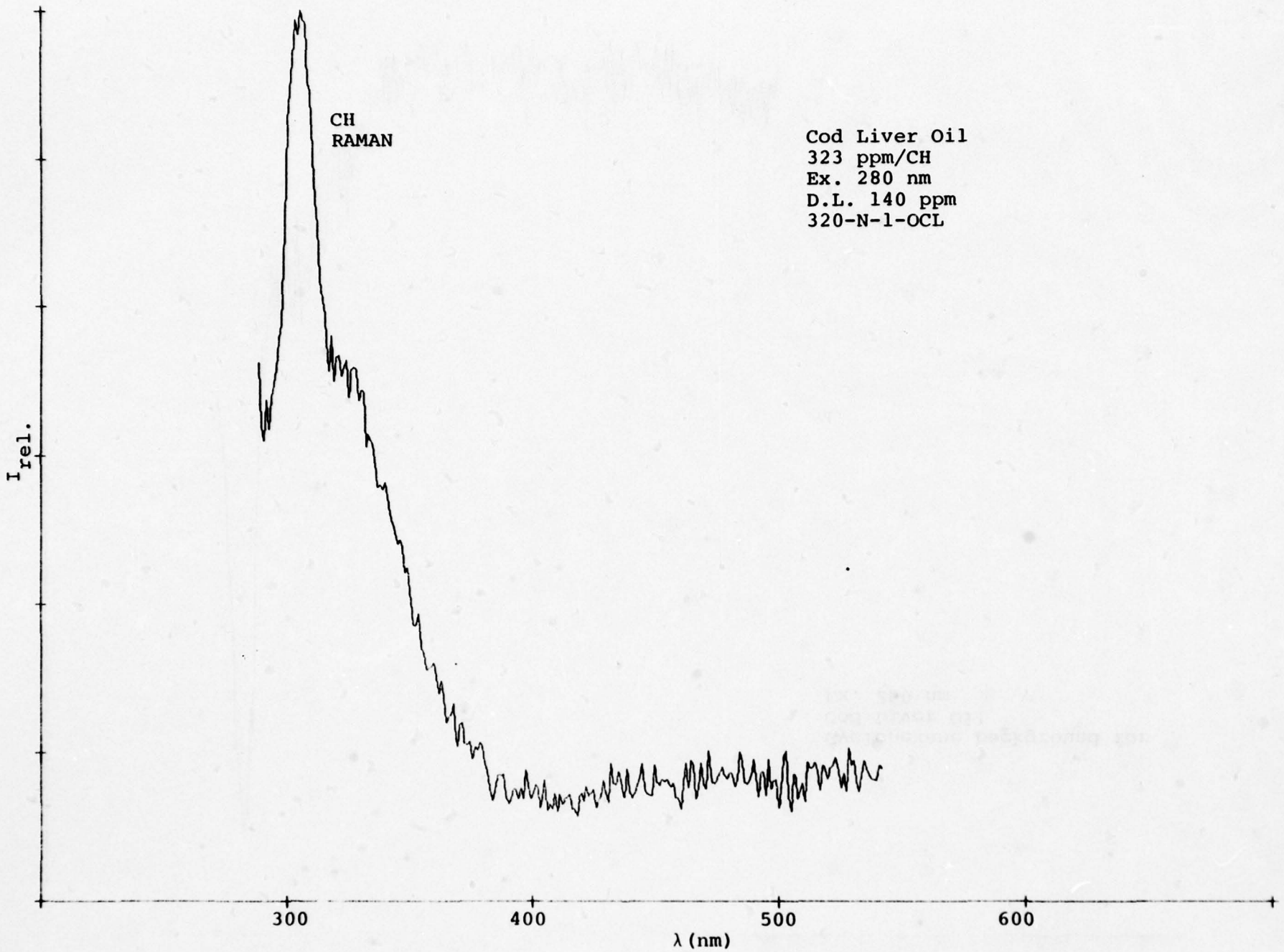

CH Raman
Coconut Oil
286 ppm/CH
Ex. 290 nm
D.L. 100 ppm
330-N-1(1)-OCC
$I_{rel.}$
300
400
500
600
λ (nm)

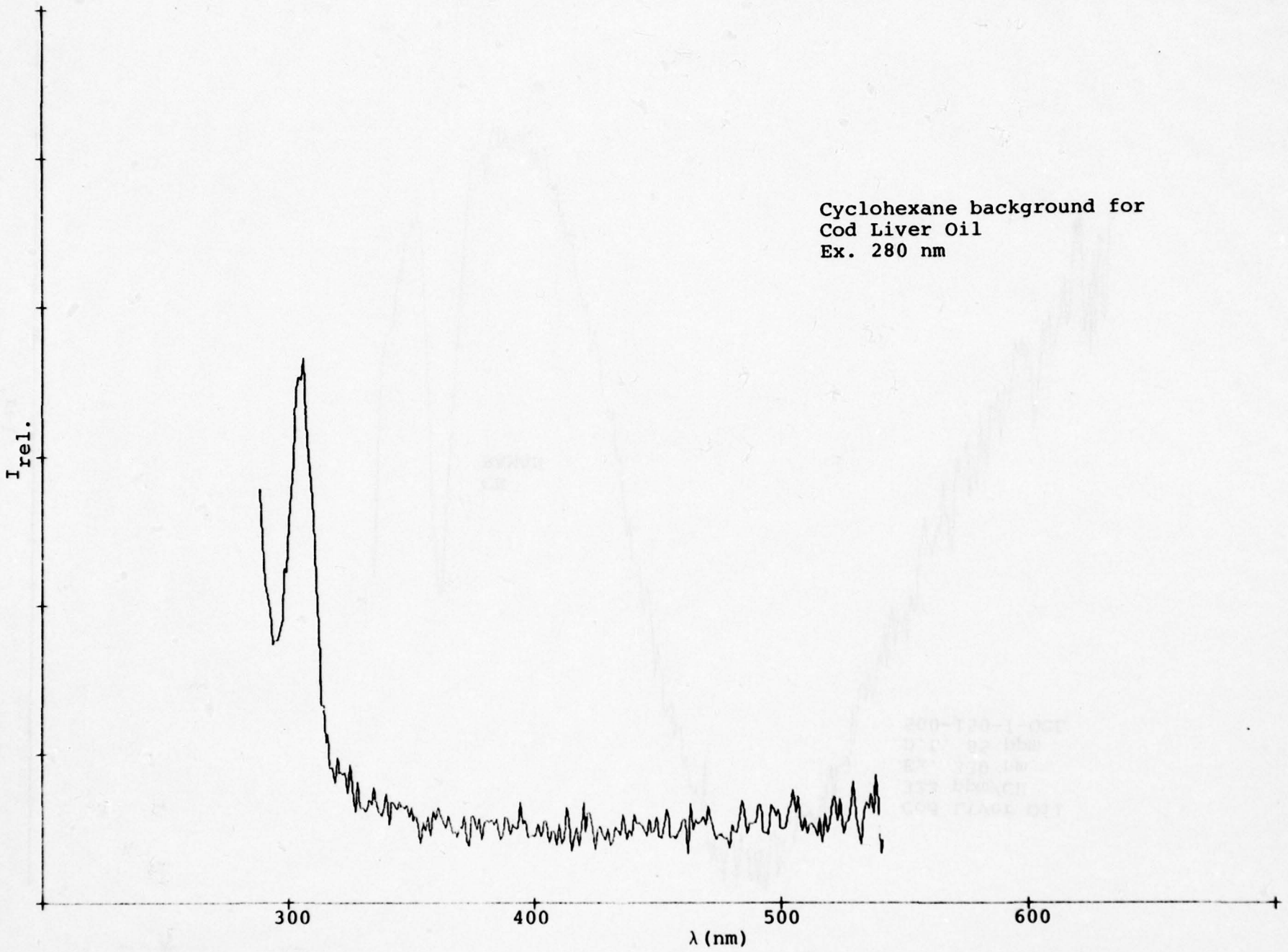
Cyclohexane background
for Coconut Oil

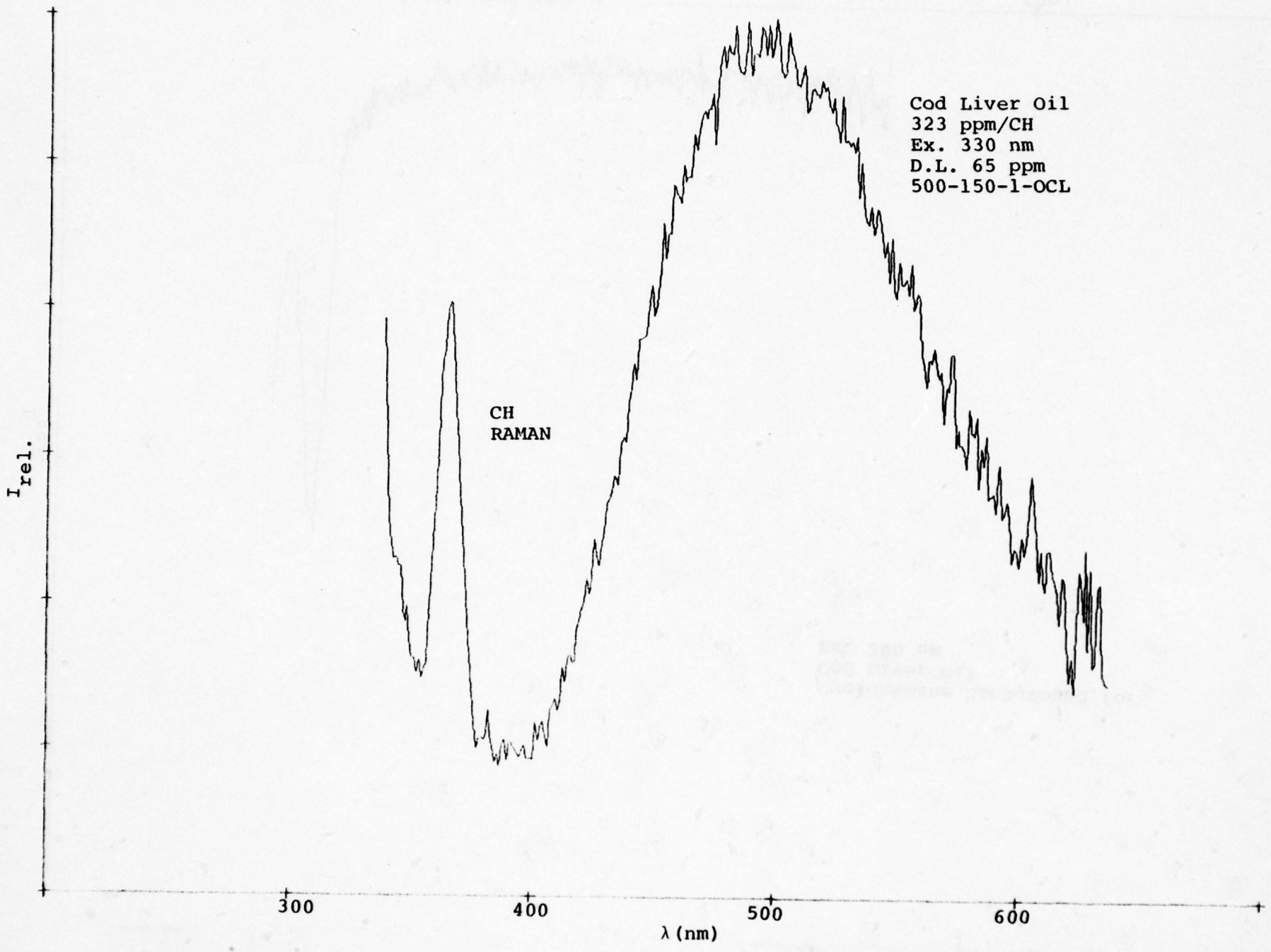


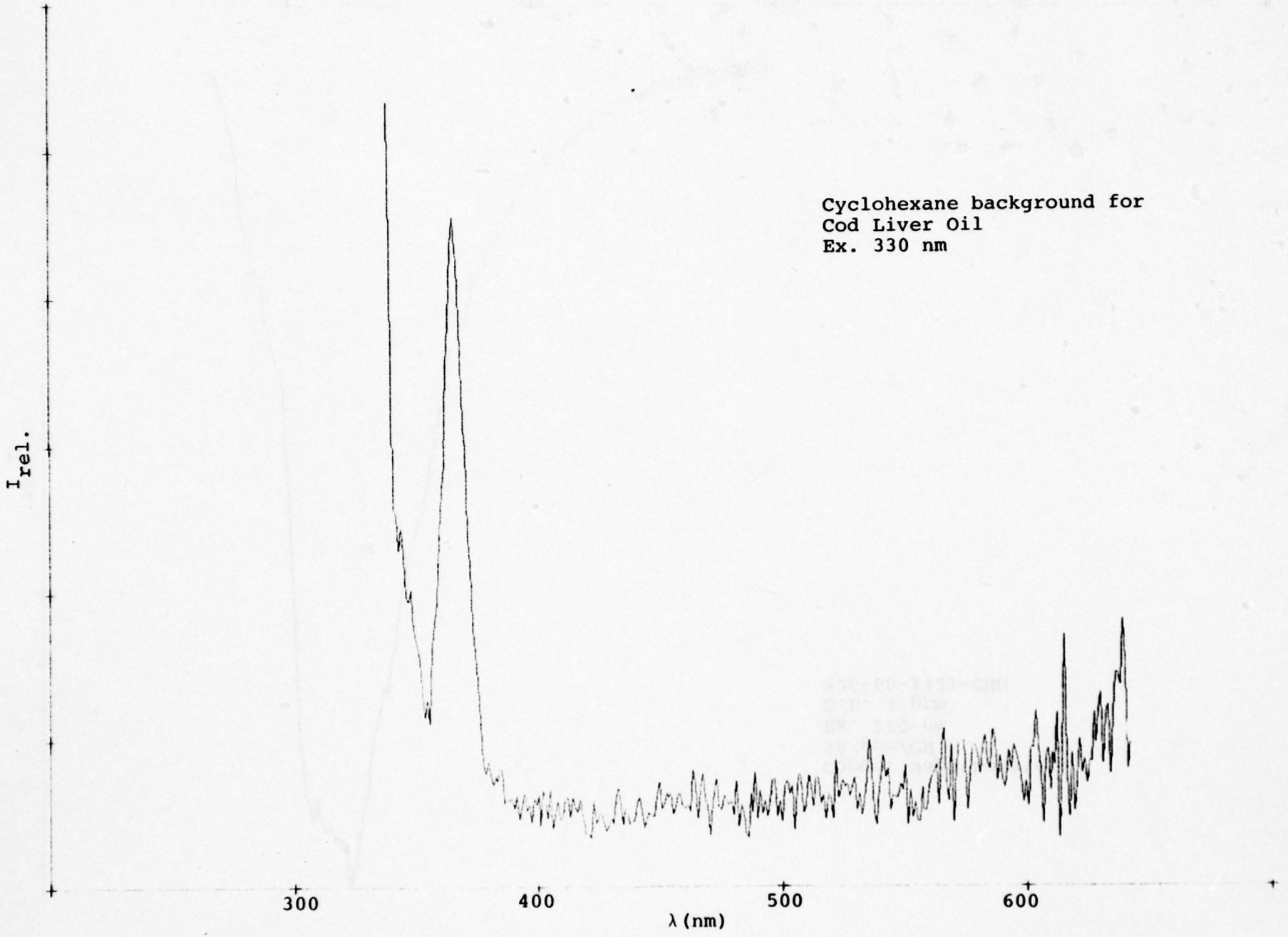

CH
RAMAN
Cod Liver Oil
323 ppm/CH
Ex. 260 nm
D.L. 260 ppm
320-N-1-OCL
$I_{rel.}$
300
400
500
600
λ (nm)

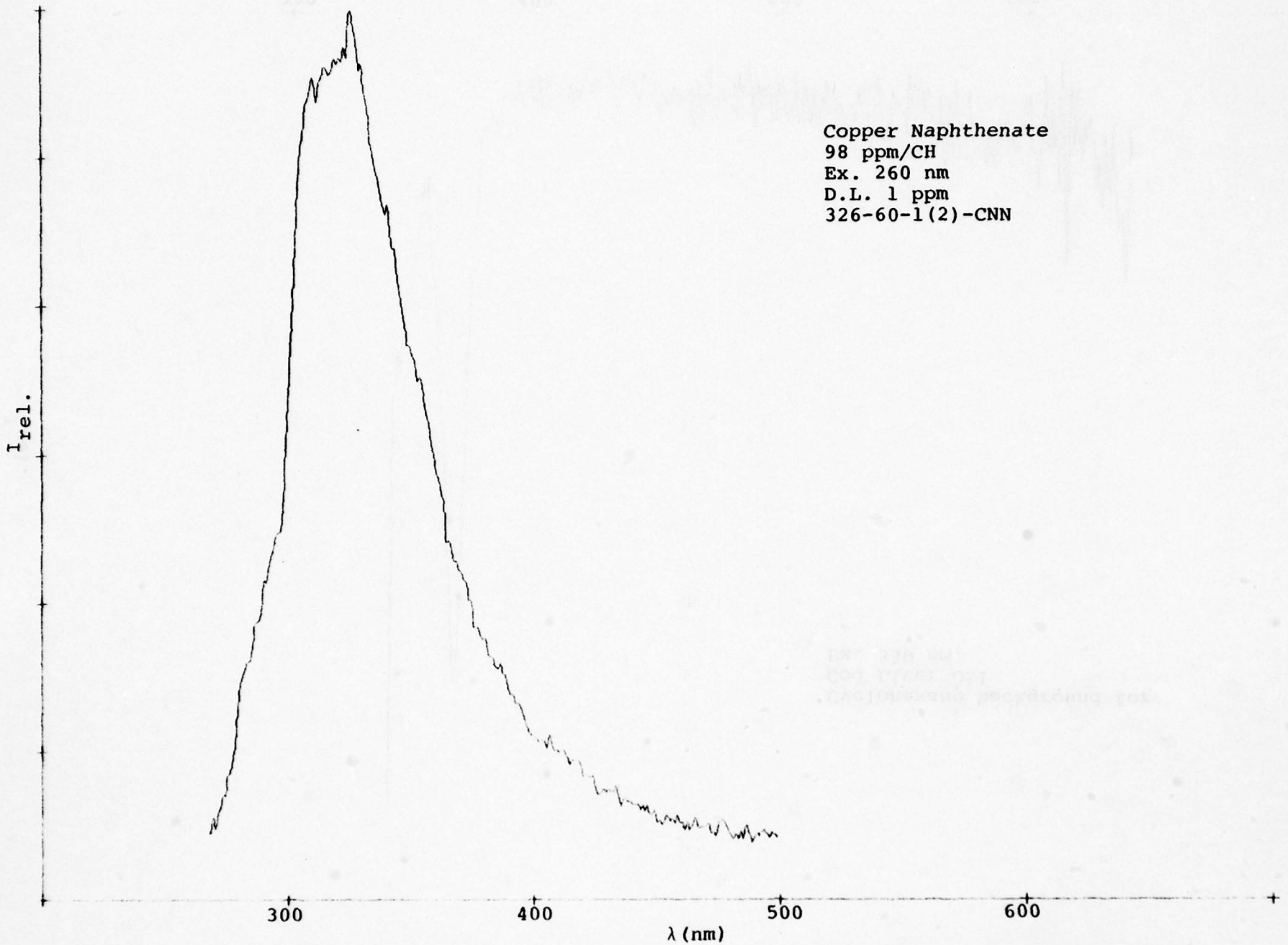

Cyclohexane background for
Cod Liver Oil
Ex. 260 nm
$I_{rel.}$
300
400
500
600
λ (nm)

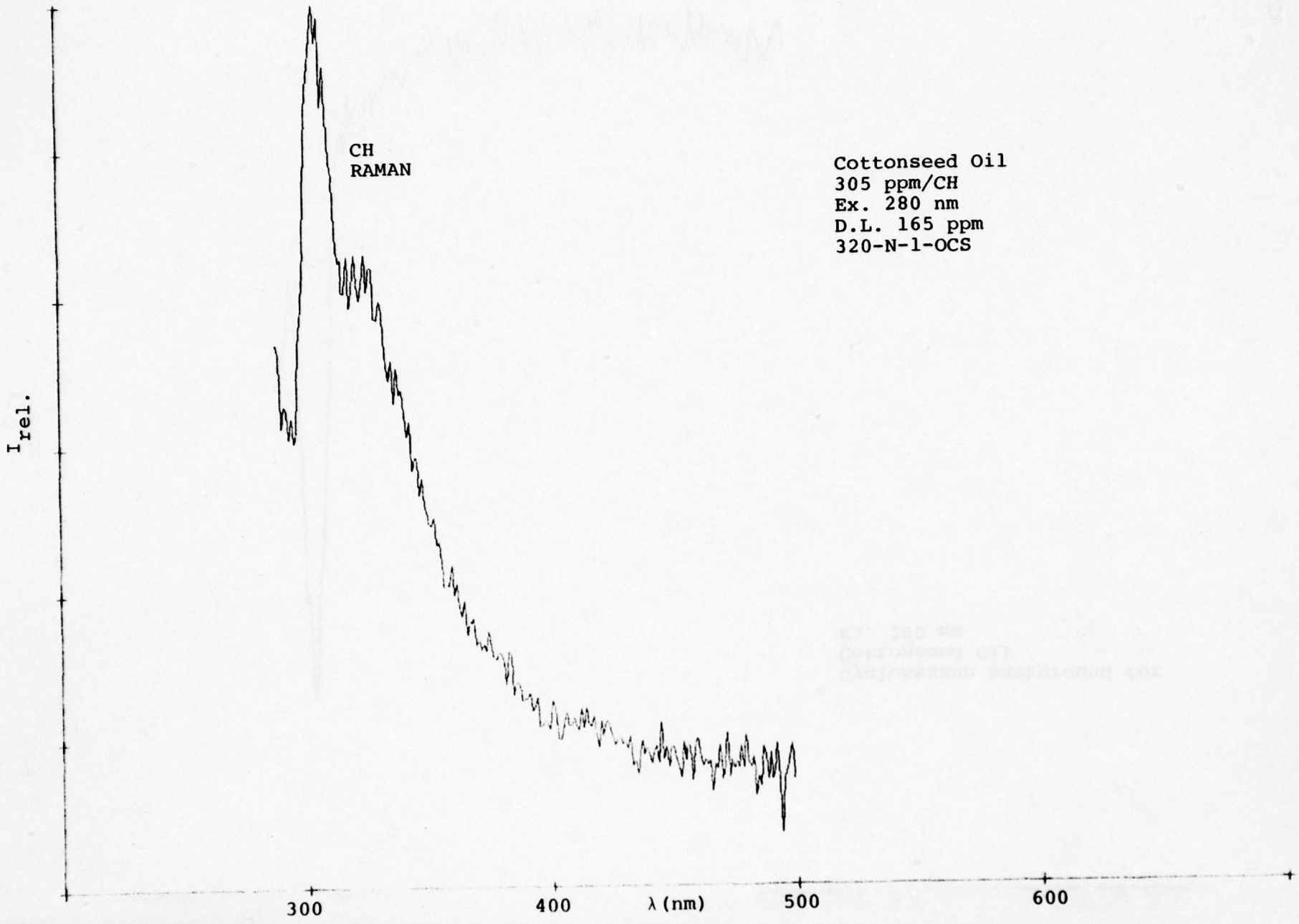

CH
RAMAN
Cod Liver Oil
323 ppm/CH
Ex. 280 nm
D.L. 140 ppm
320-N-1-OCL
Irel.
300
400
500
600
λ (nm)

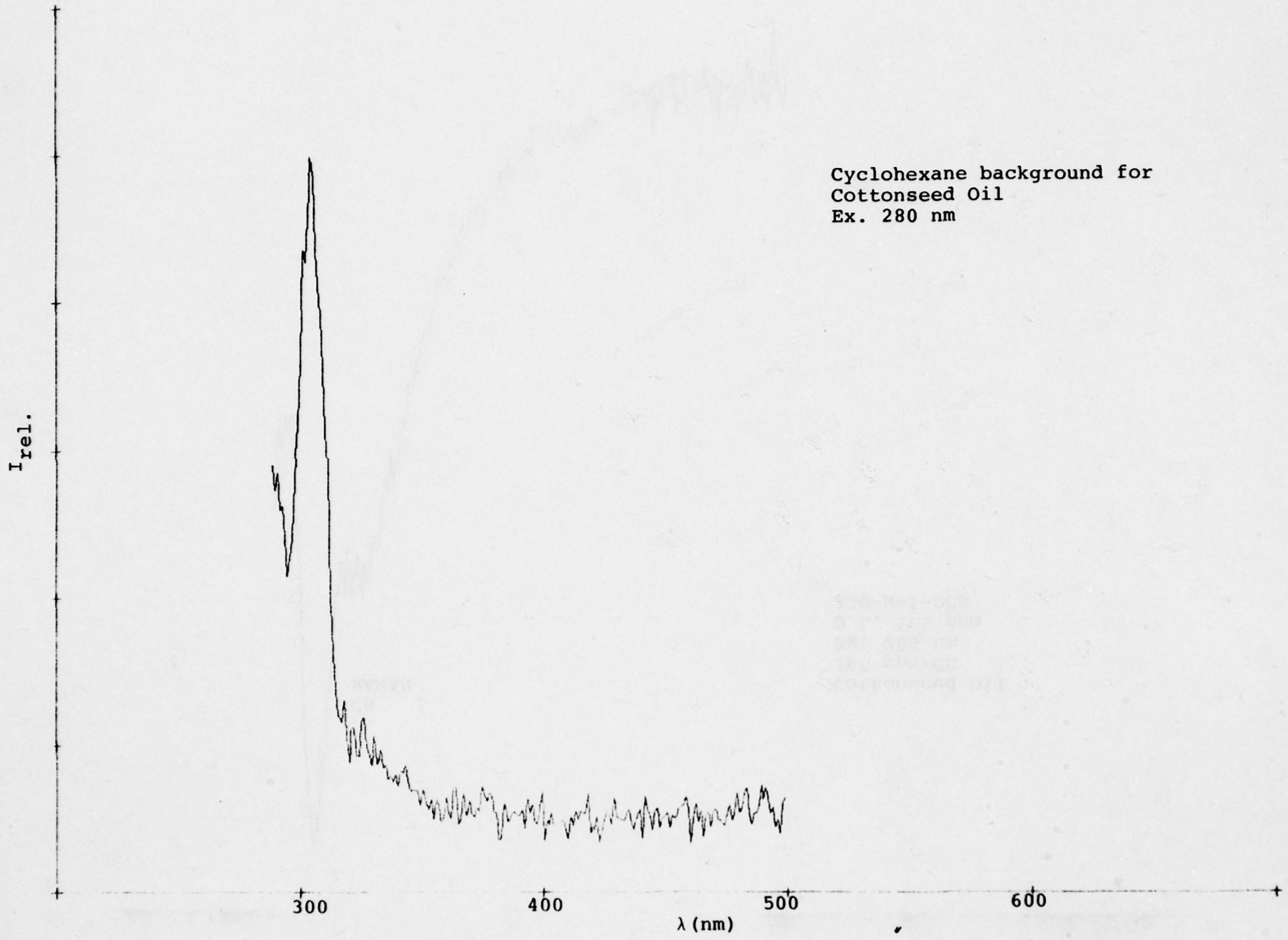

Cyclohexane background for
Cod Liver Oil
Ex. 280 nm
I rel.
300
400
500
600
λ (nm)

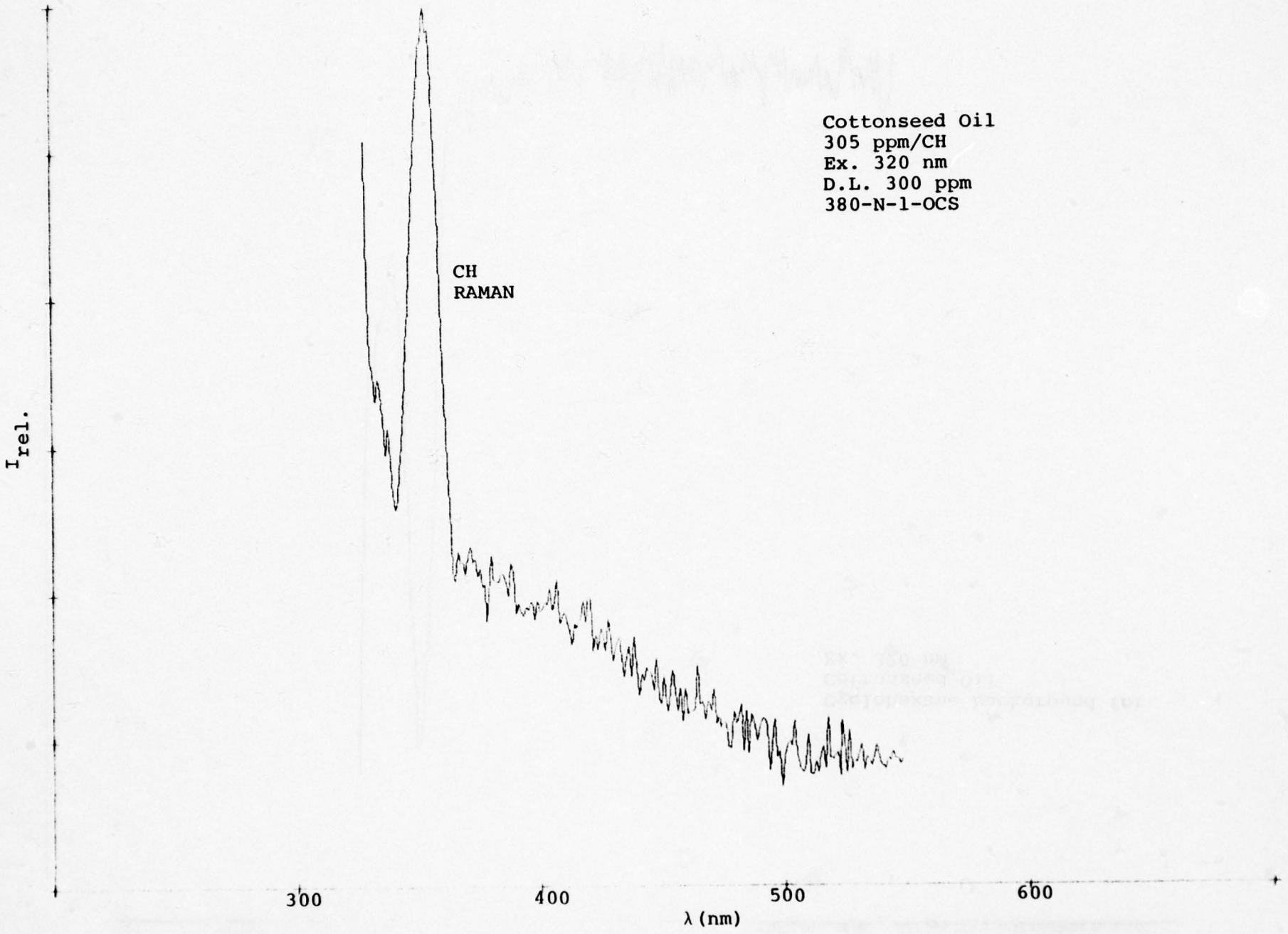

Cod Liver Oil
323 ppm/CH
Ex. 330 nm
D.L. 65 ppm
500-150-1-OCL
CH
RAMAN
$I_{rel.}$
300
400
500
600
λ (nm)

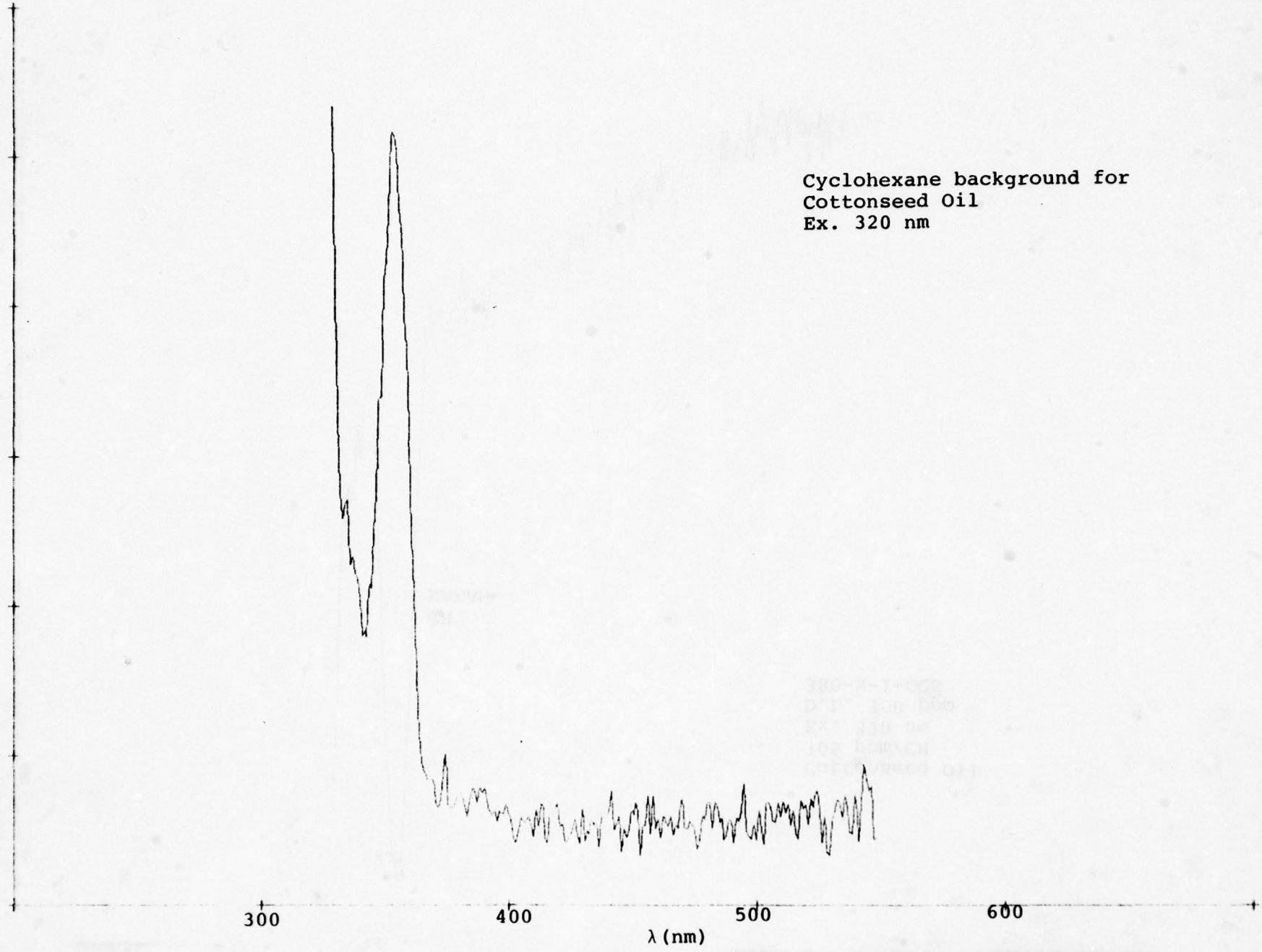

Cyclohexane background for
Cod Liver Oil
Ex. 330 nm
$I_{rel.}$
300
400
500
600
λ (nm)


Copper Naphthenate
98 ppm/CH
Ex. 260 nm
D.L. 1 ppm
326-60-1(2)-CNN
I rel.
300
400
500
600
λ (nm)

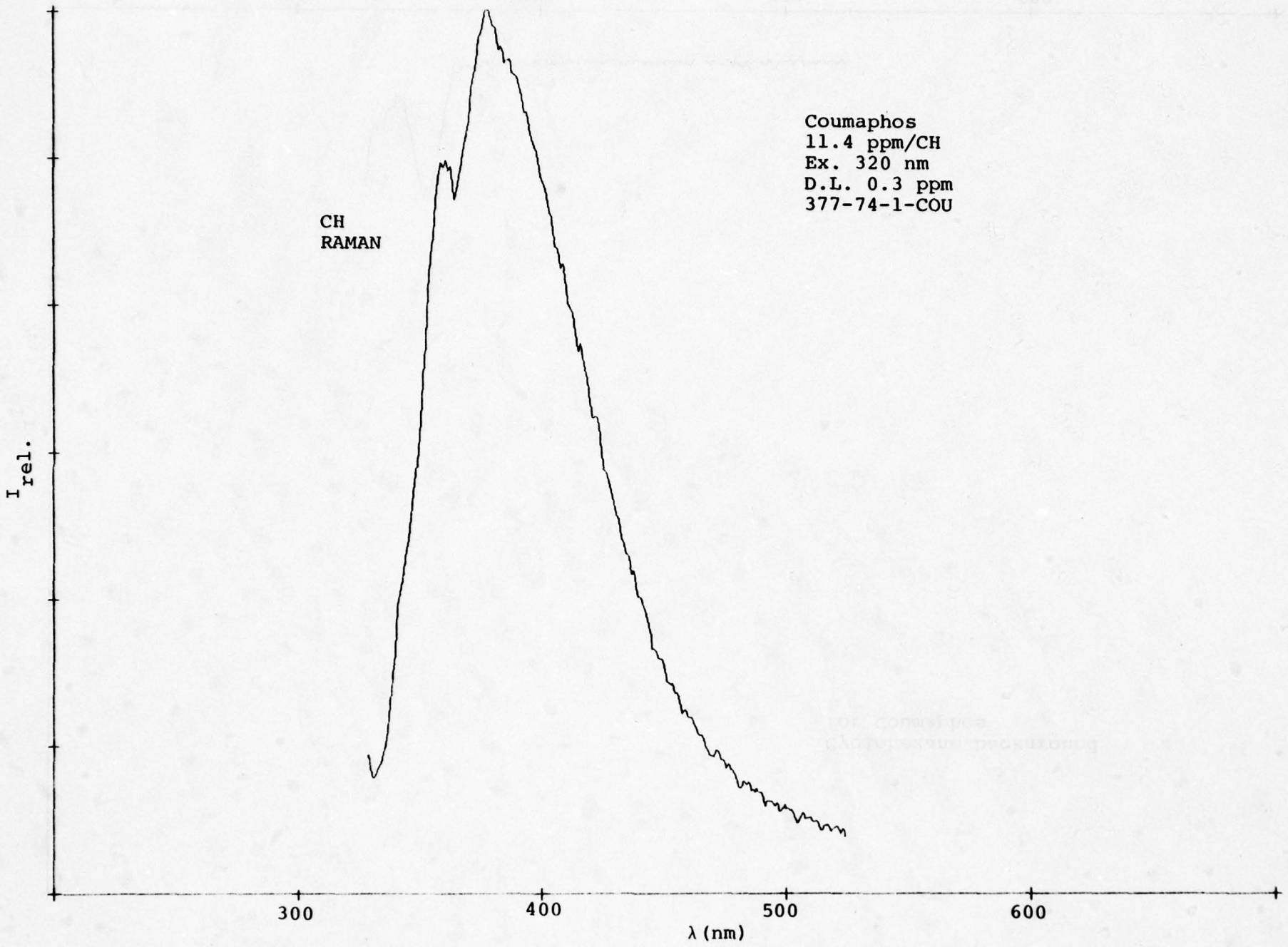

CH
RAMAN
Cottonseed Oil
305 ppm/CH
Ex. 280 nm
D.L. 165 ppm
320-N-1-OCS
$I_{rel.}$
300
400
λ (nm)
500
600


Cyclohexane background for
Cottonseed Oil
Ex. 280 nm
$I_{rel.}$
300
400
500
600
λ (nm)

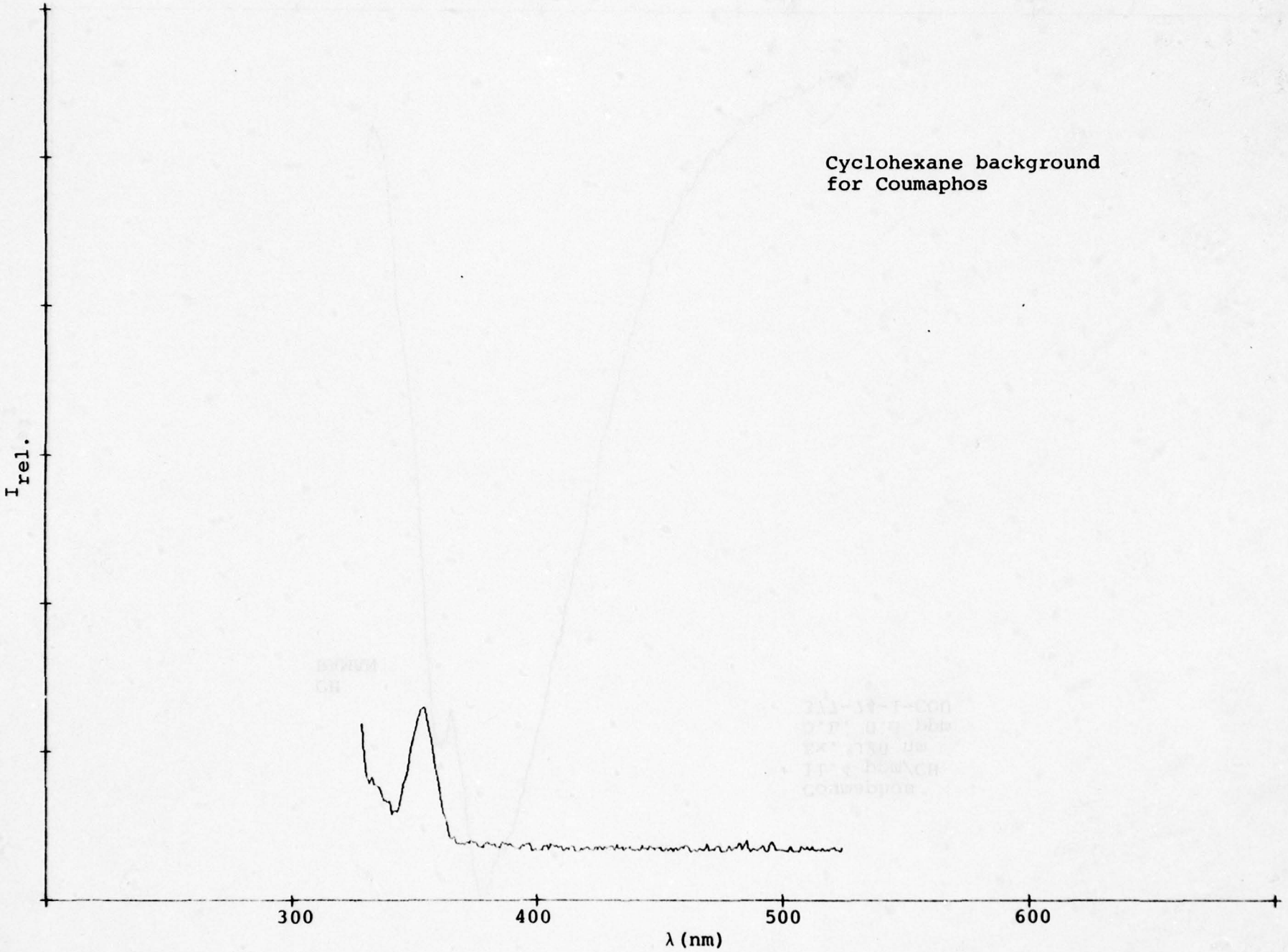

Cottonseed Oil
305 ppm/CH
Ex. 320 nm
D.L. 300 ppm
380-N-1-OCS
CH
RAMAN
$I_{rel.}$
300
400
500
600
λ (nm)

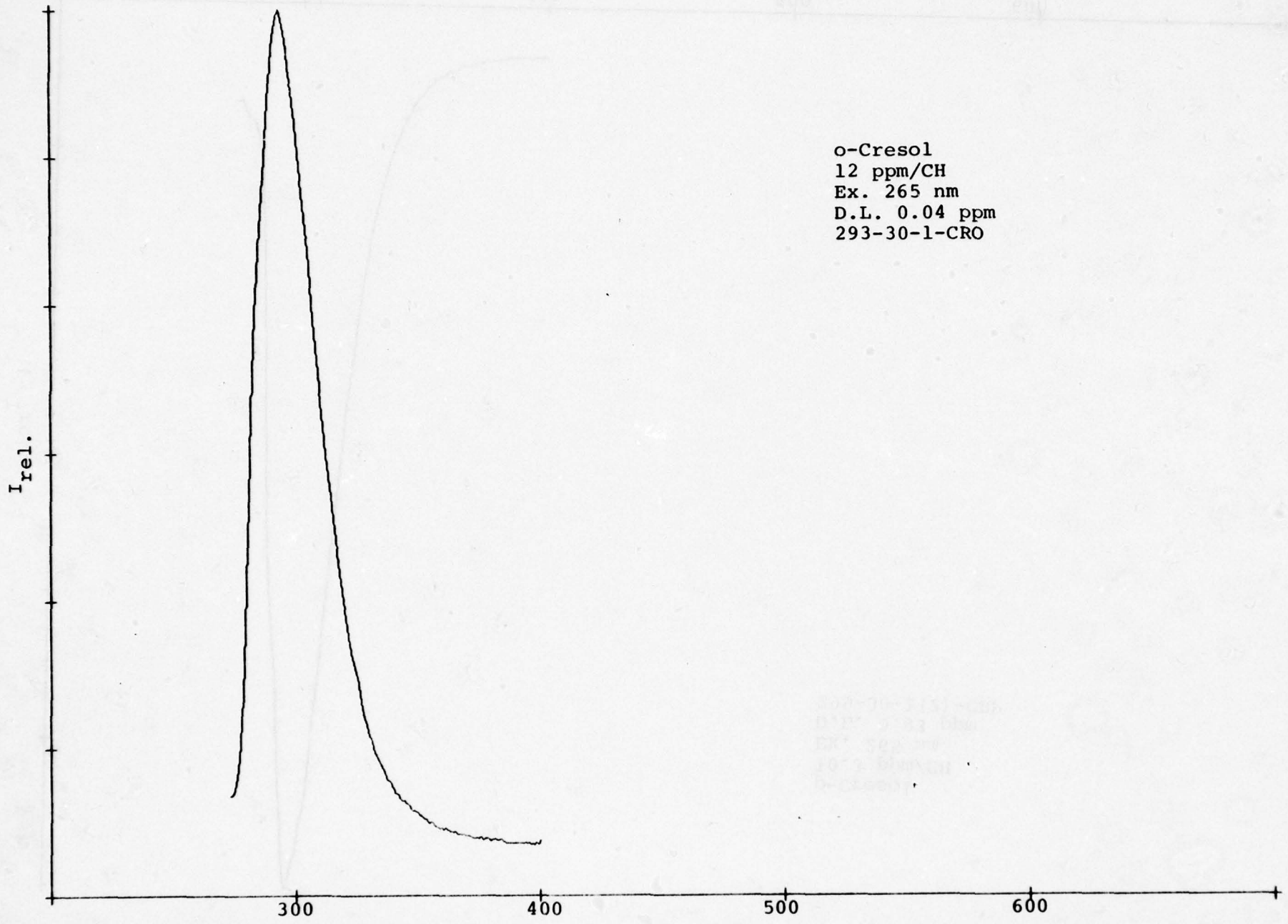


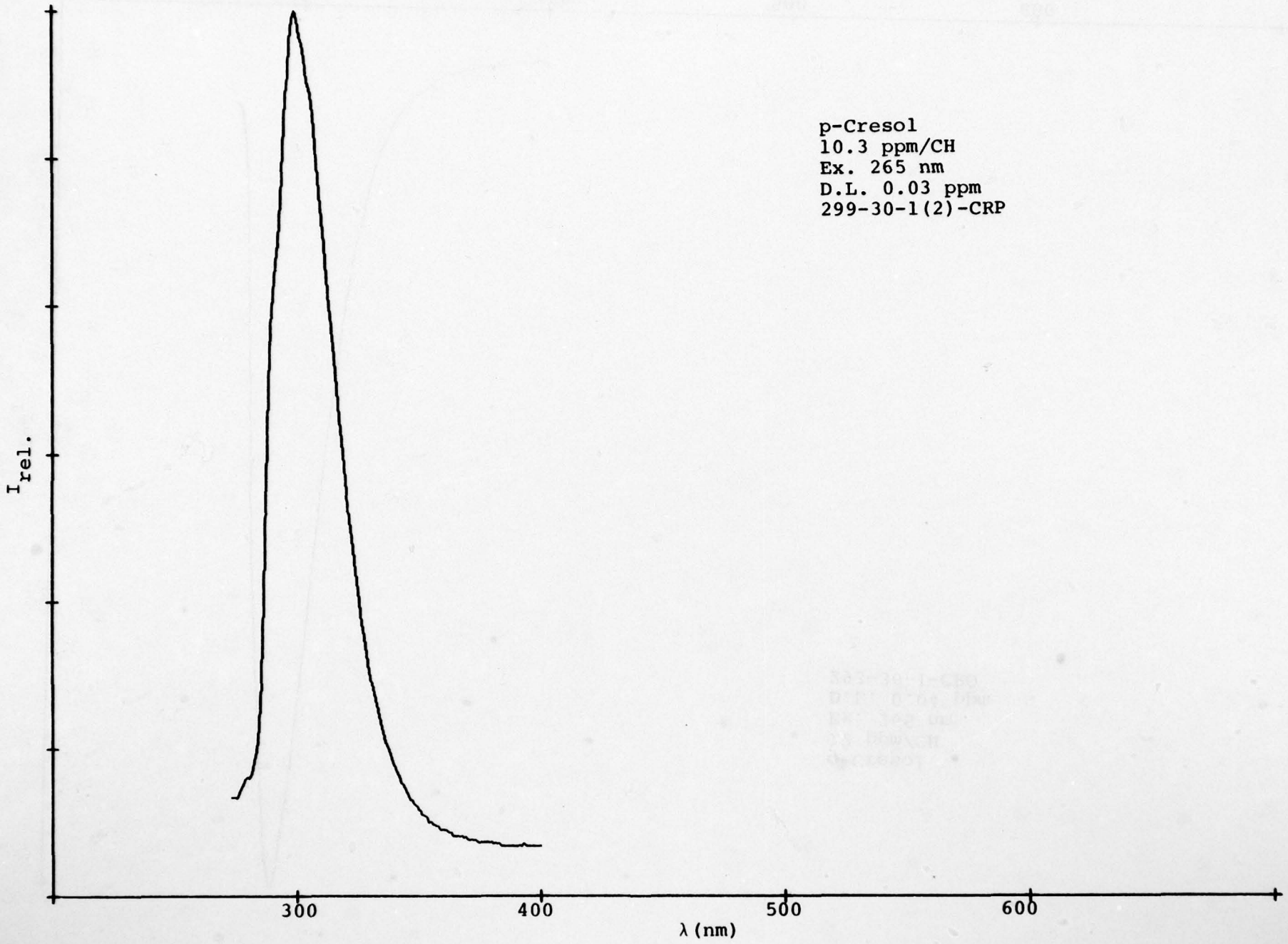
Cyclohexane background for
Cottonseed Oil
Ex. 320 nm

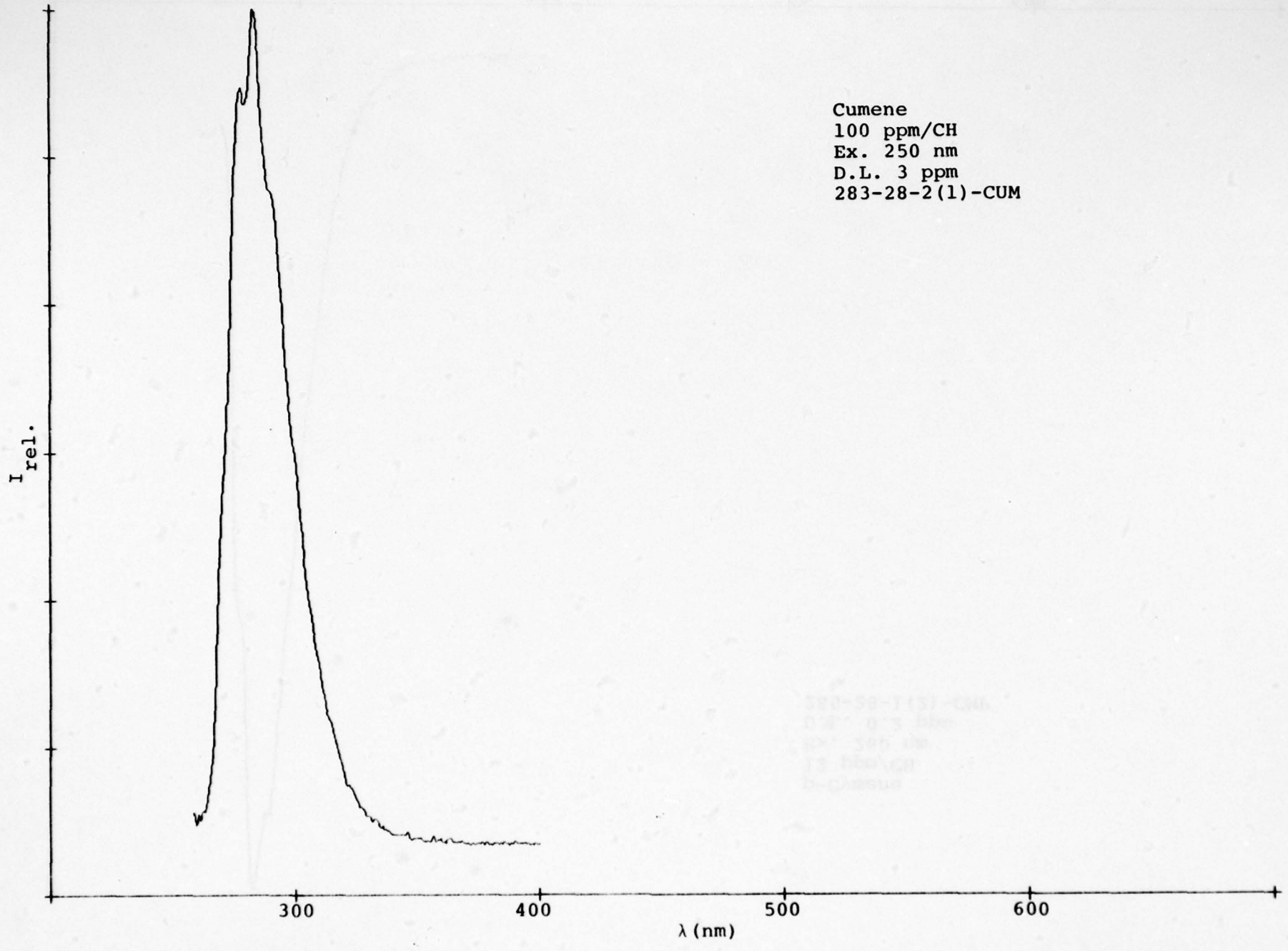

Coumaphos
11.4 ppm/CH
Ex. 320 nm
D.L. 0.3 ppm
377-74-1-COU
CH
RAMAN
I rel.
300
400
500
600
λ (nm)

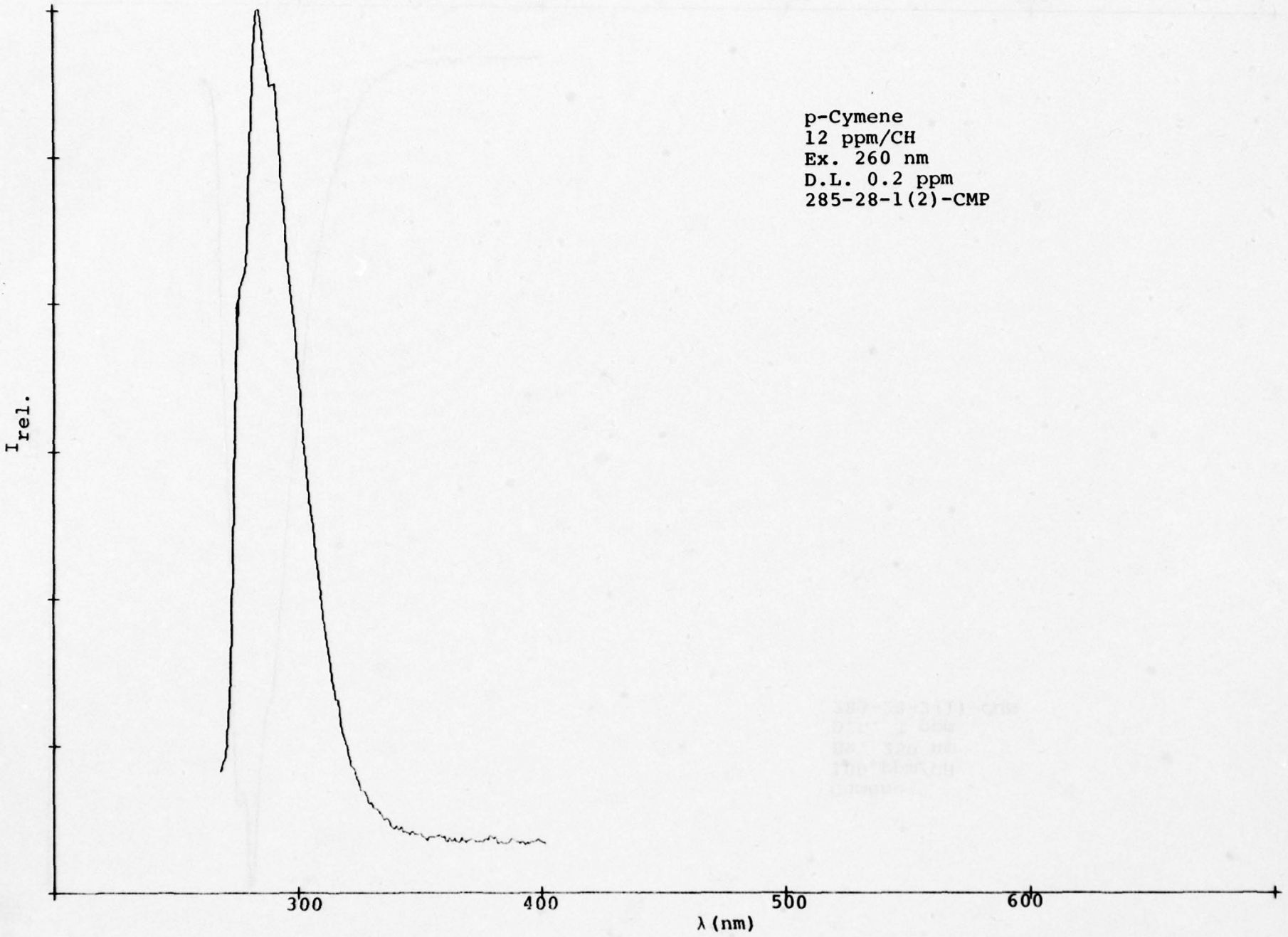
Cyclohexane background
for Coumaphos

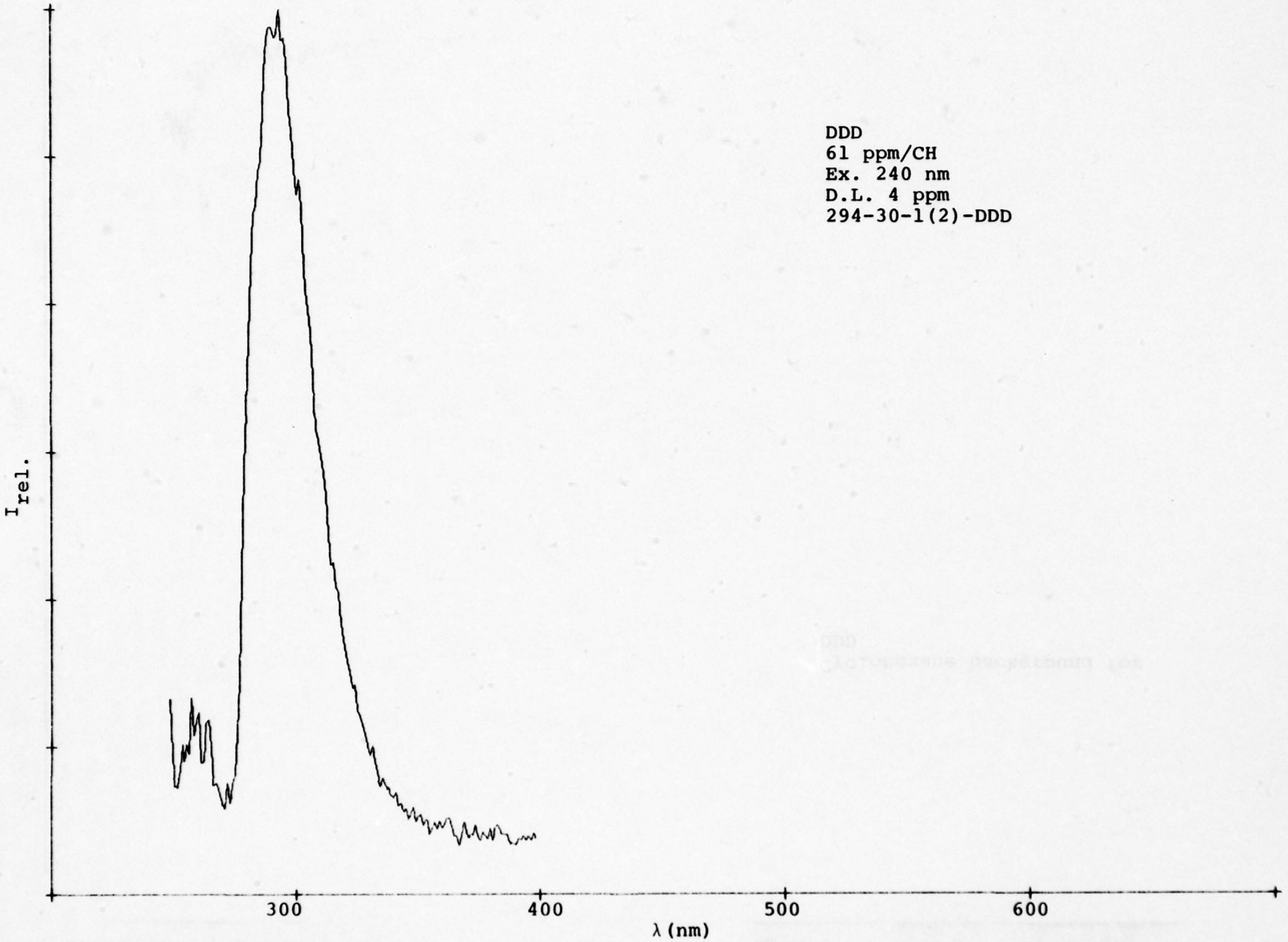



o-Cresol
12 ppm/CH
Ex. 265 nm
D.L. 0.04 ppm
293-30-1-CRO
$I_{rel.}$
300
400
500
600

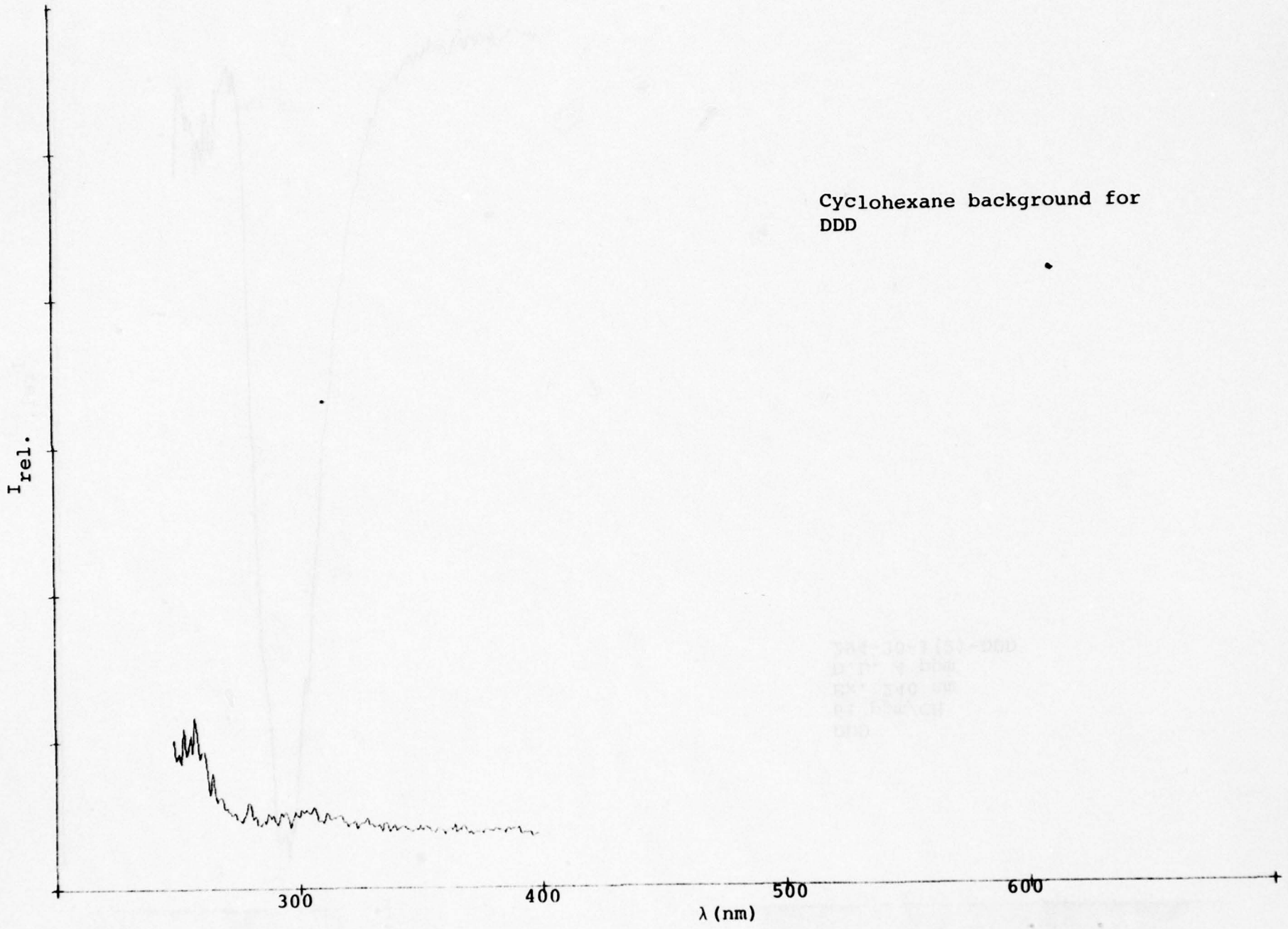

p-Cresol
10.3 ppm/CH
Ex. 265 nm
D.L. 0.03 ppm
299-30-1(2)-CRP
$I_{rel.}$
300
400
500
600
λ (nm)

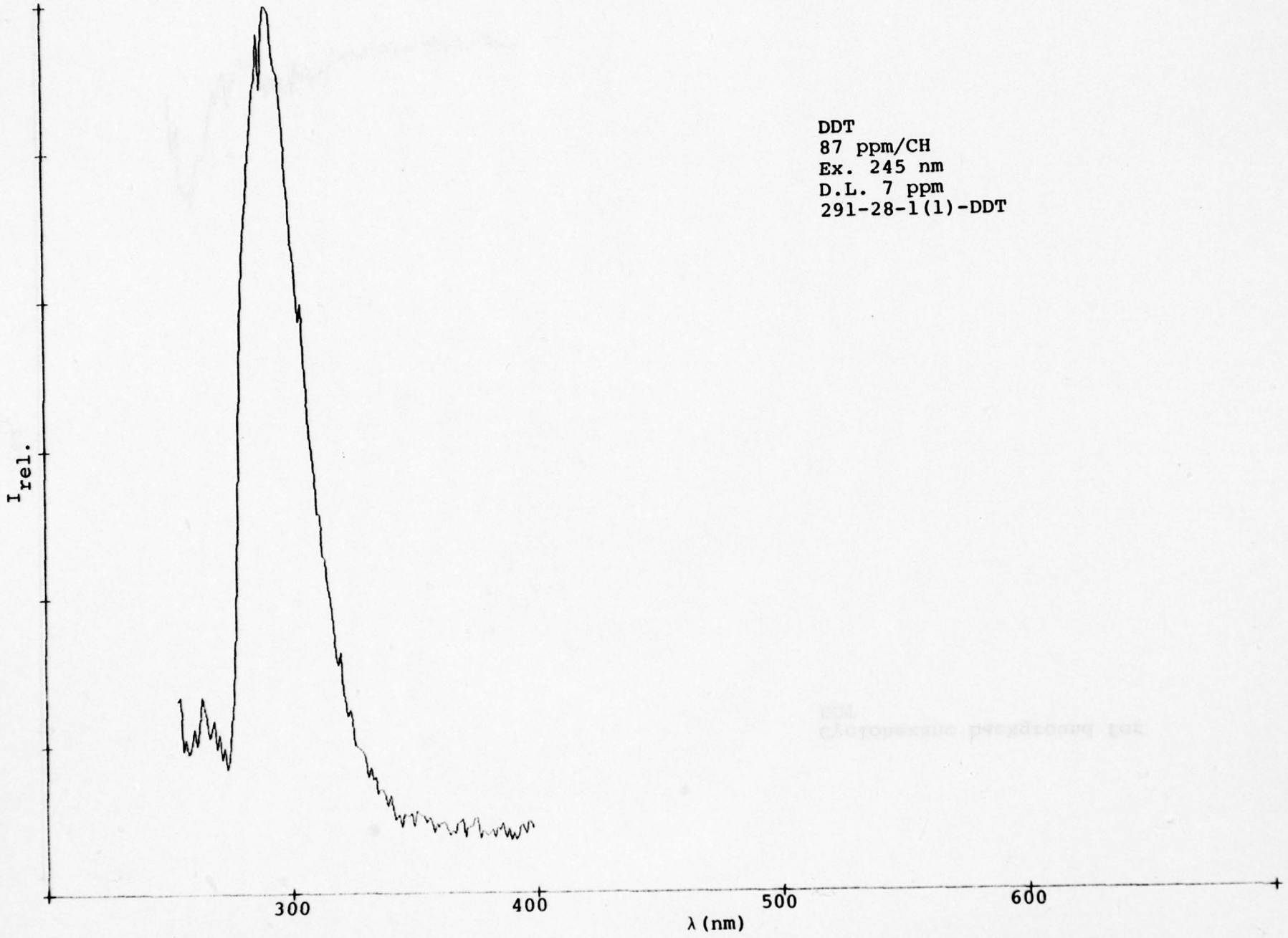

Cumene
100 ppm/CH
Ex. 250 nm
D.L. 3 ppm
283-28-2(1)-CUM
I rel.
300
400
500
600
λ (nm)


p-Cymene
12 ppm/CH
Ex. 260 nm
D.L. 0.2 ppm
285-28-1(2)-CMP
$I_{rel.}$
300
400
500
600
λ (nm)

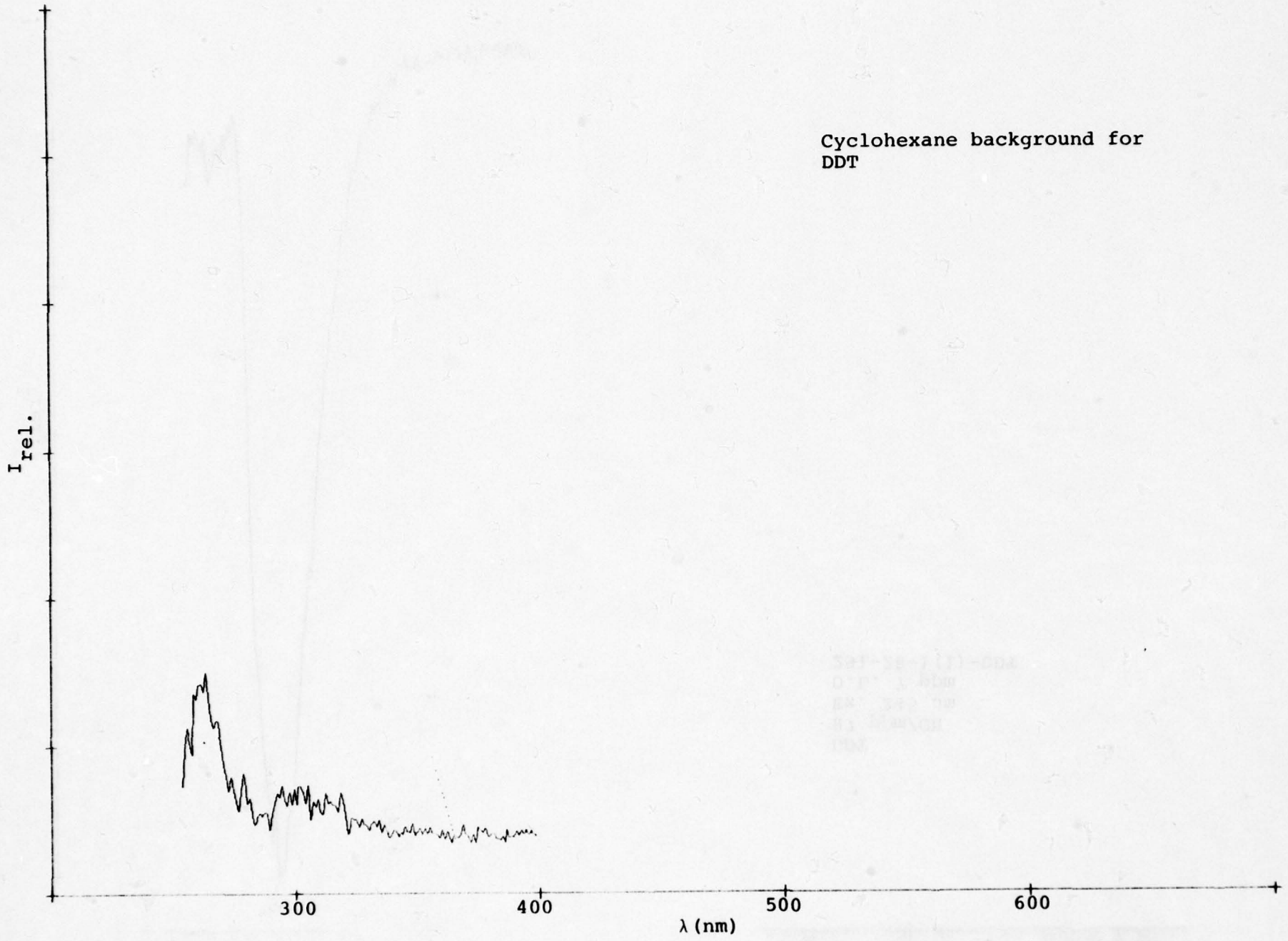

DDD
61 ppm/CH
Ex. 240 nm
D.L. 4 ppm
294-30-1(2)-DDD
I rel.
300
400
500
600
λ (nm)

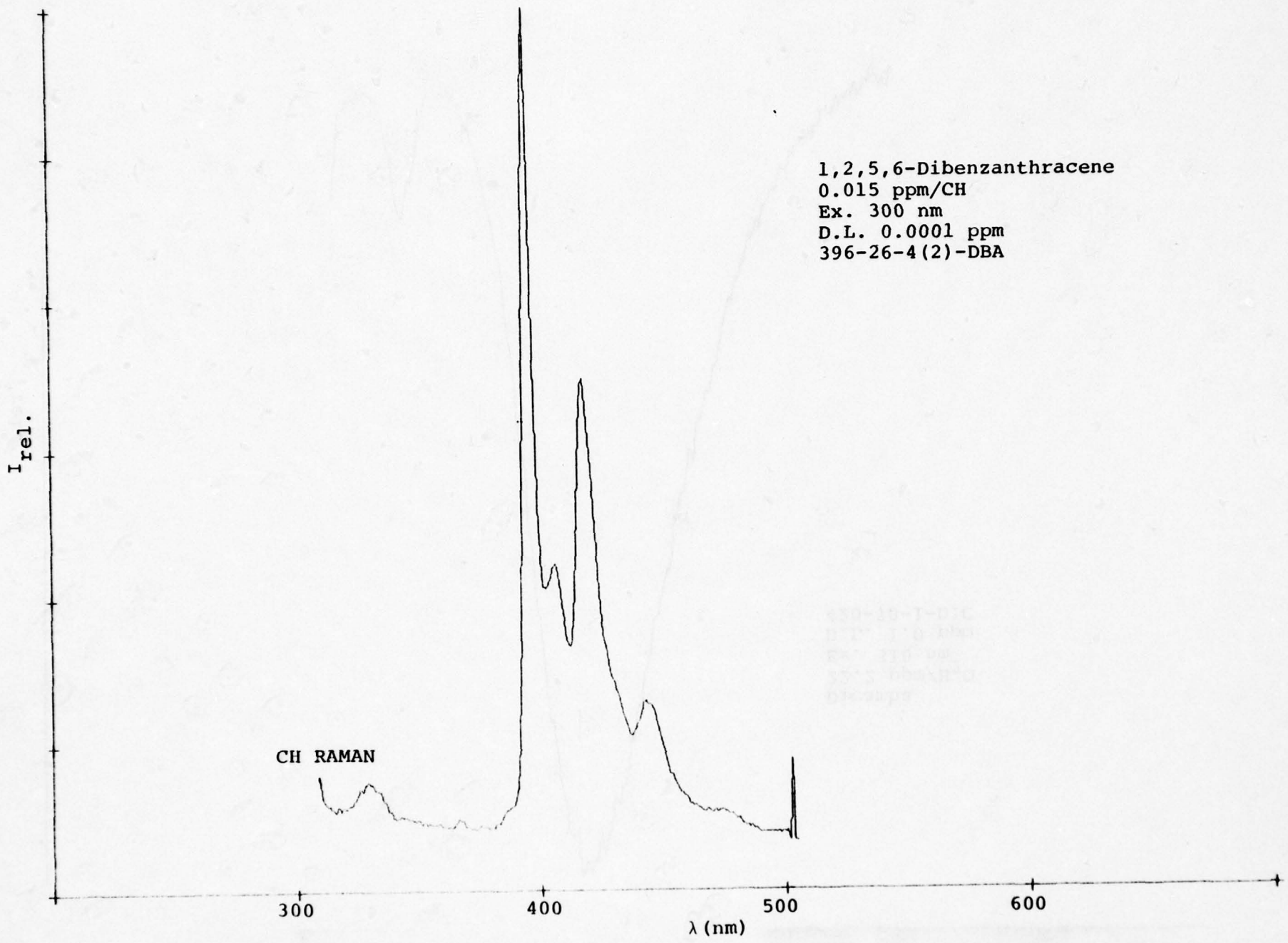
Cyclohexane background for DDD

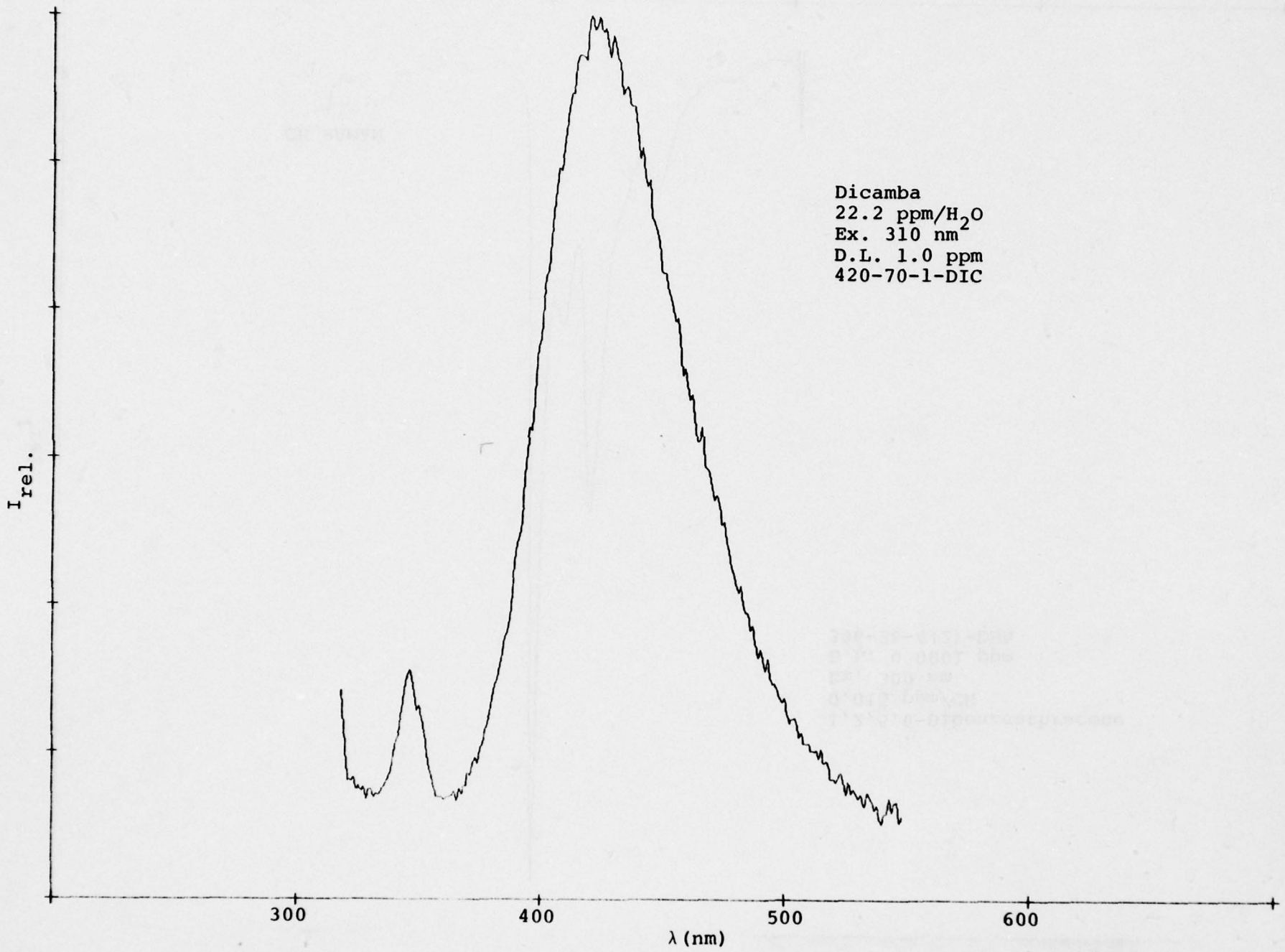


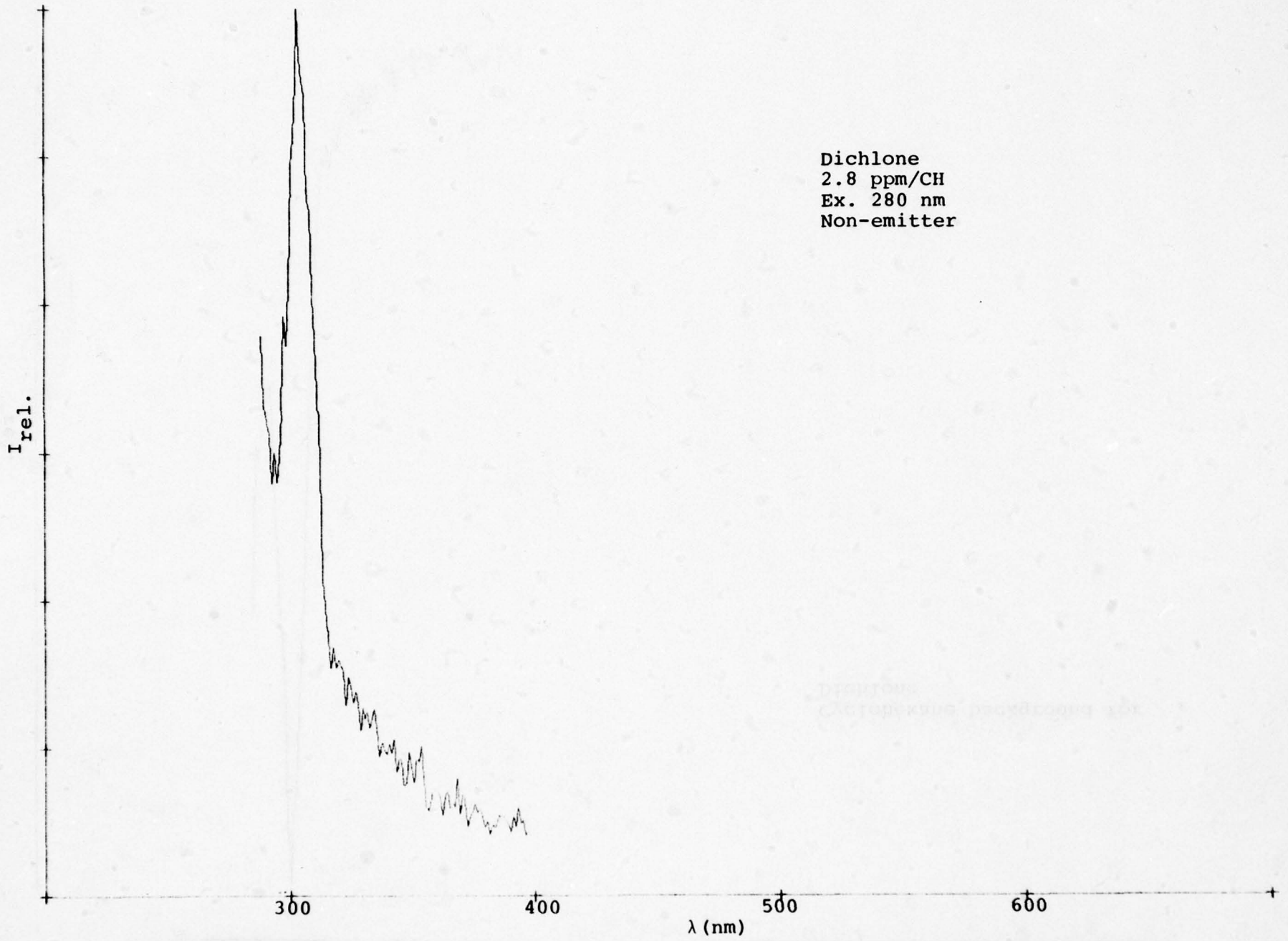

DDT
87 ppm/CH
Ex. 245 nm
D.L. 7 ppm
291-28-1(1)-DDT
I rel.
300
400
500
600
λ (nm)

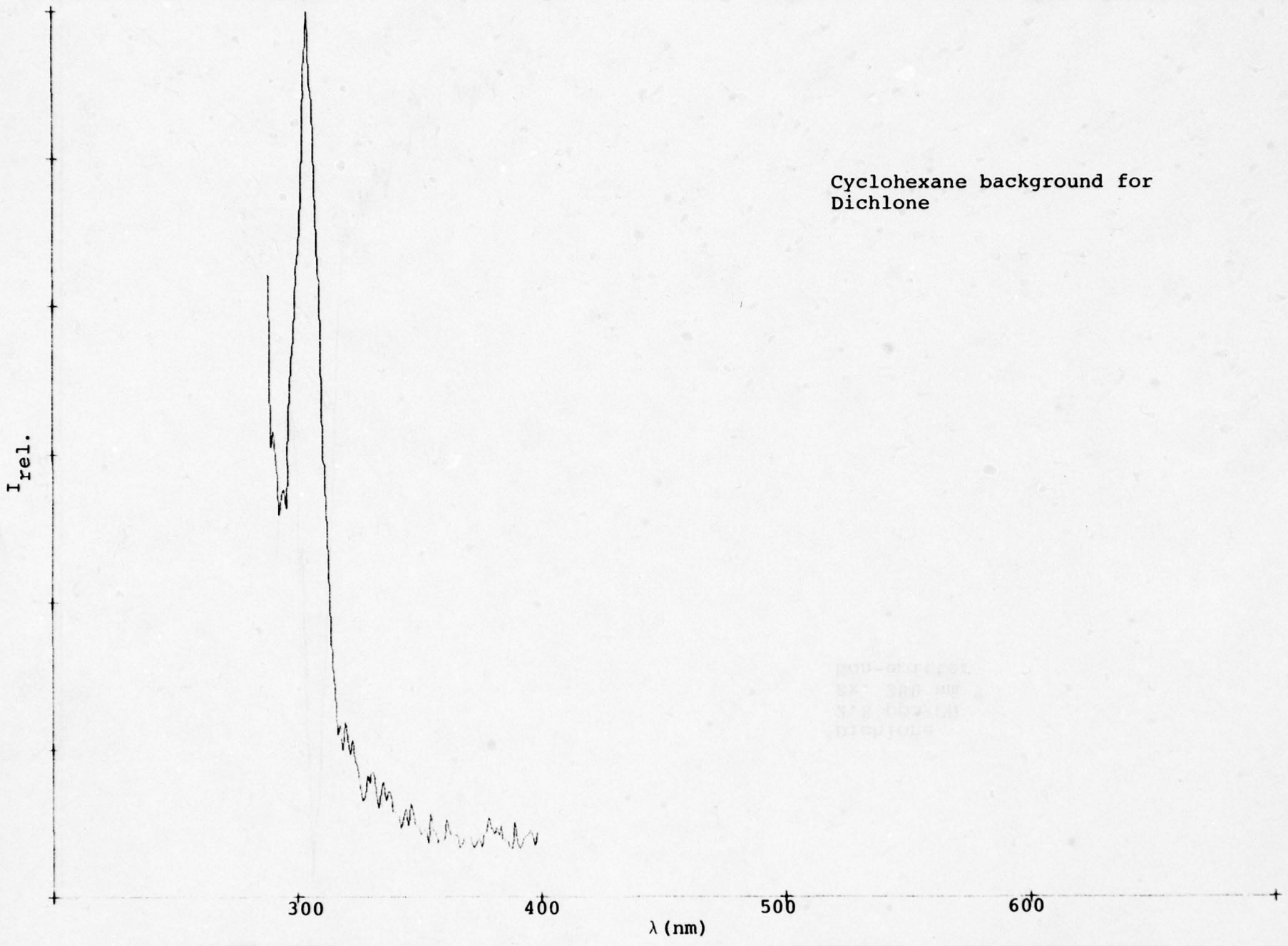
Cyclohexane background for
DDT



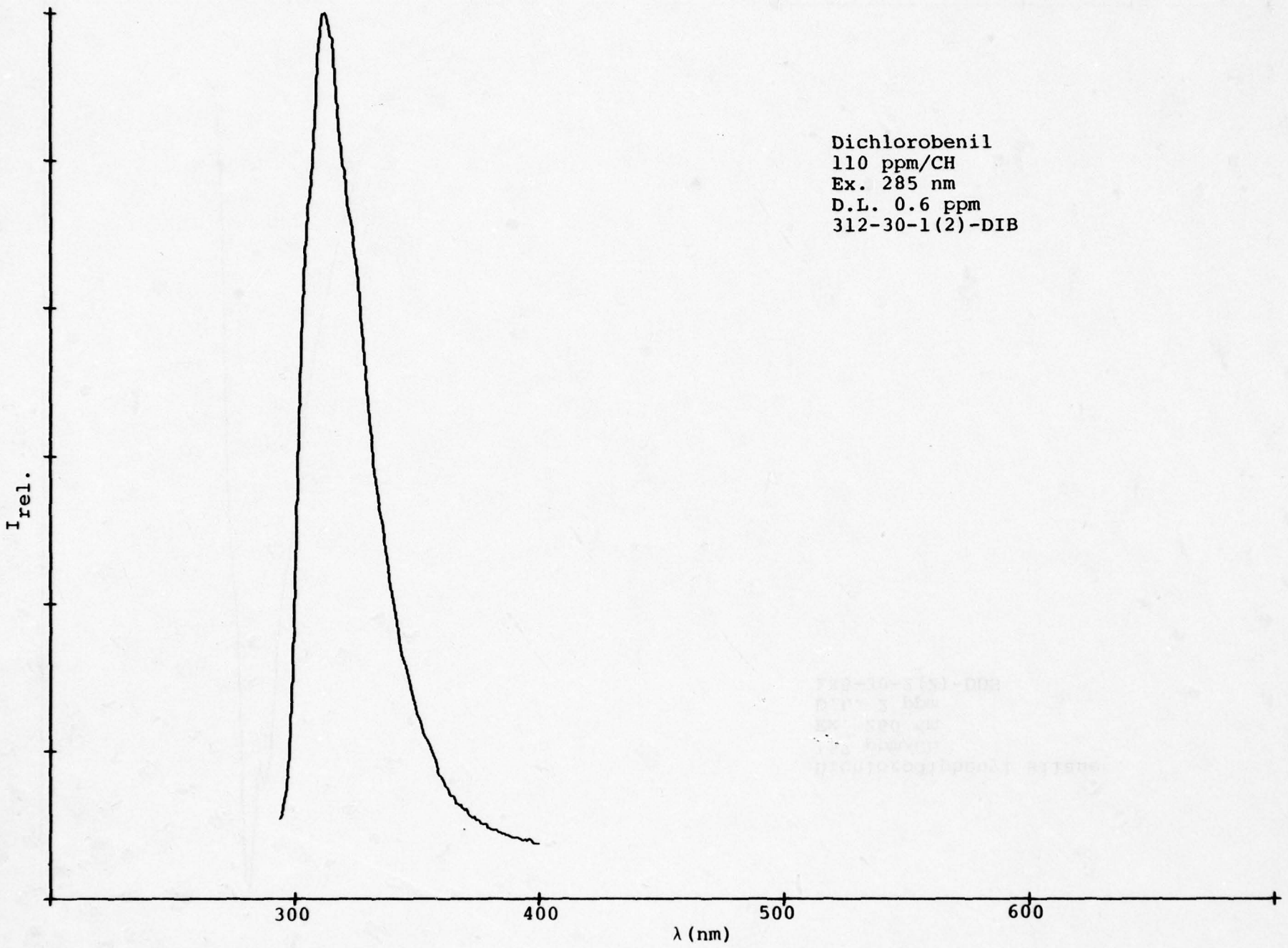

1,2,5,6-Dibenzanthracene
0.015 ppm/CH
Ex. 300 nm
D.L. 0.0001 ppm
396-26-4(2)-DBA
$I_{rel.}$
CH RAMAN
300
400
500
600
λ (nm)

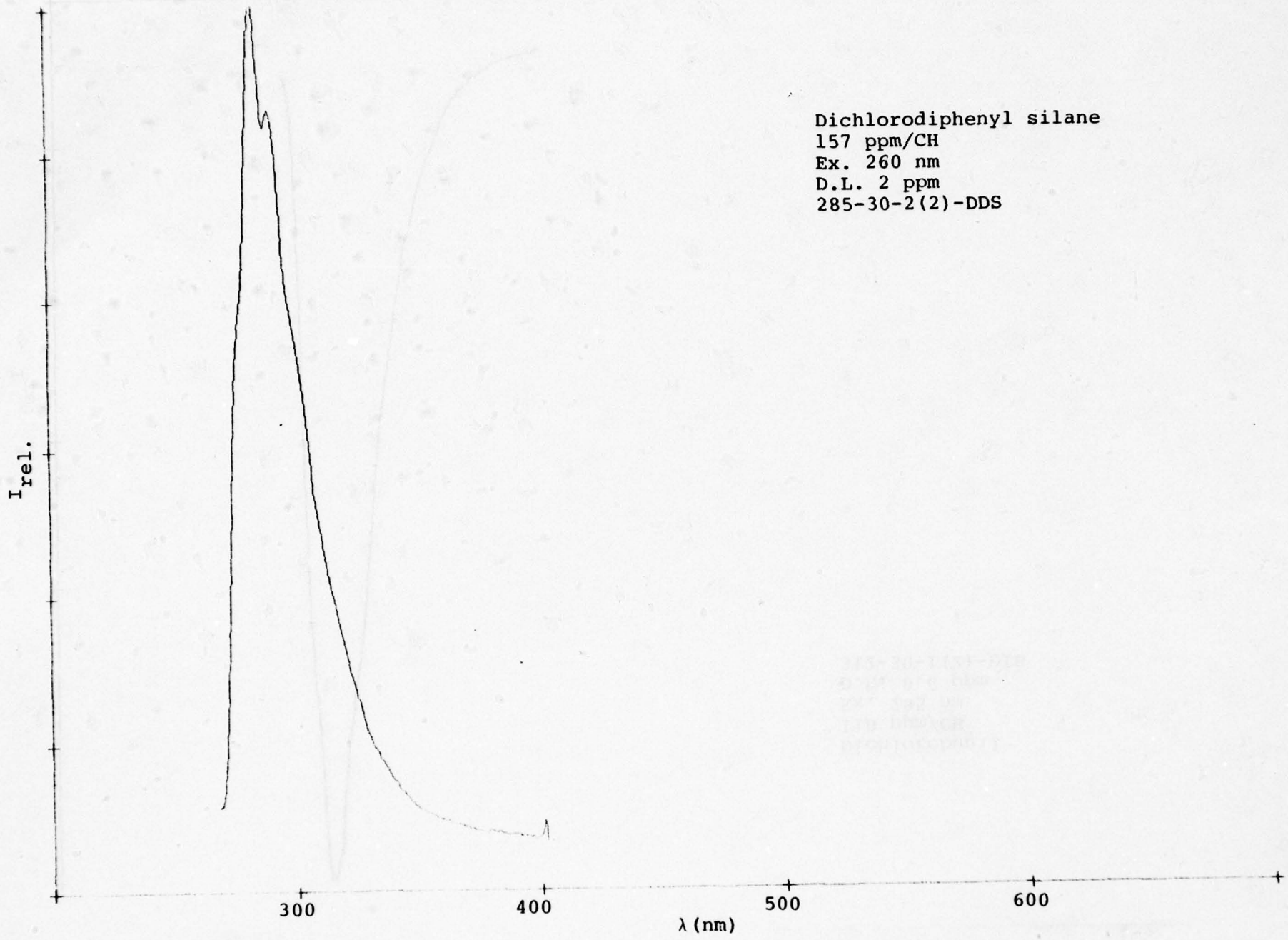

Dicamba
22.2 ppm/H_2O
Ex. 310 nm
D.L. 1.0 ppm
420-70-1-DIC
$I_{rel.}$
300
400
500
600
λ (nm)

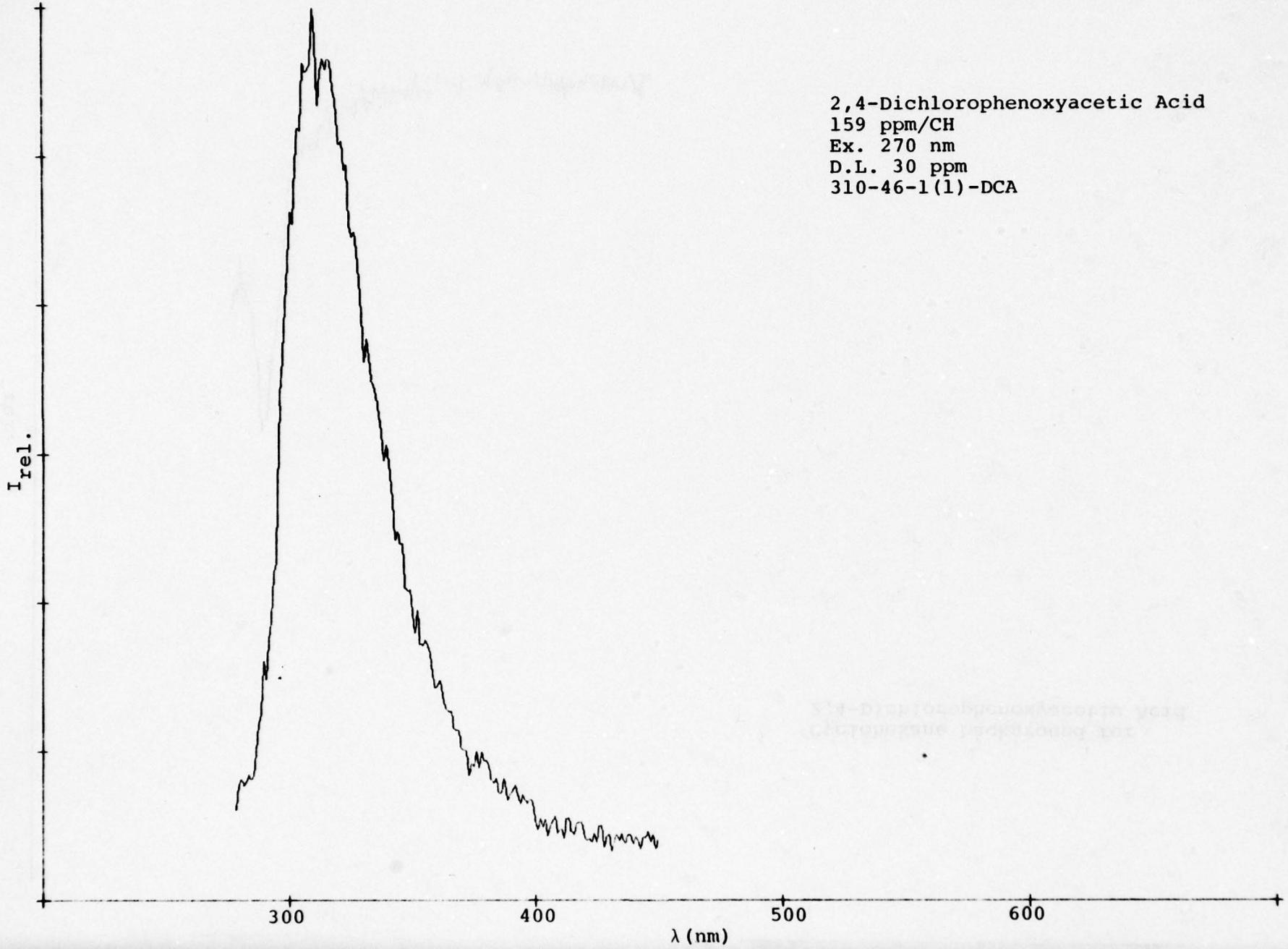

Dichlone
2.8 ppm/CH
Ex. 280 nm
Non-emitter
I rel.
300
400
500
600
λ (nm)



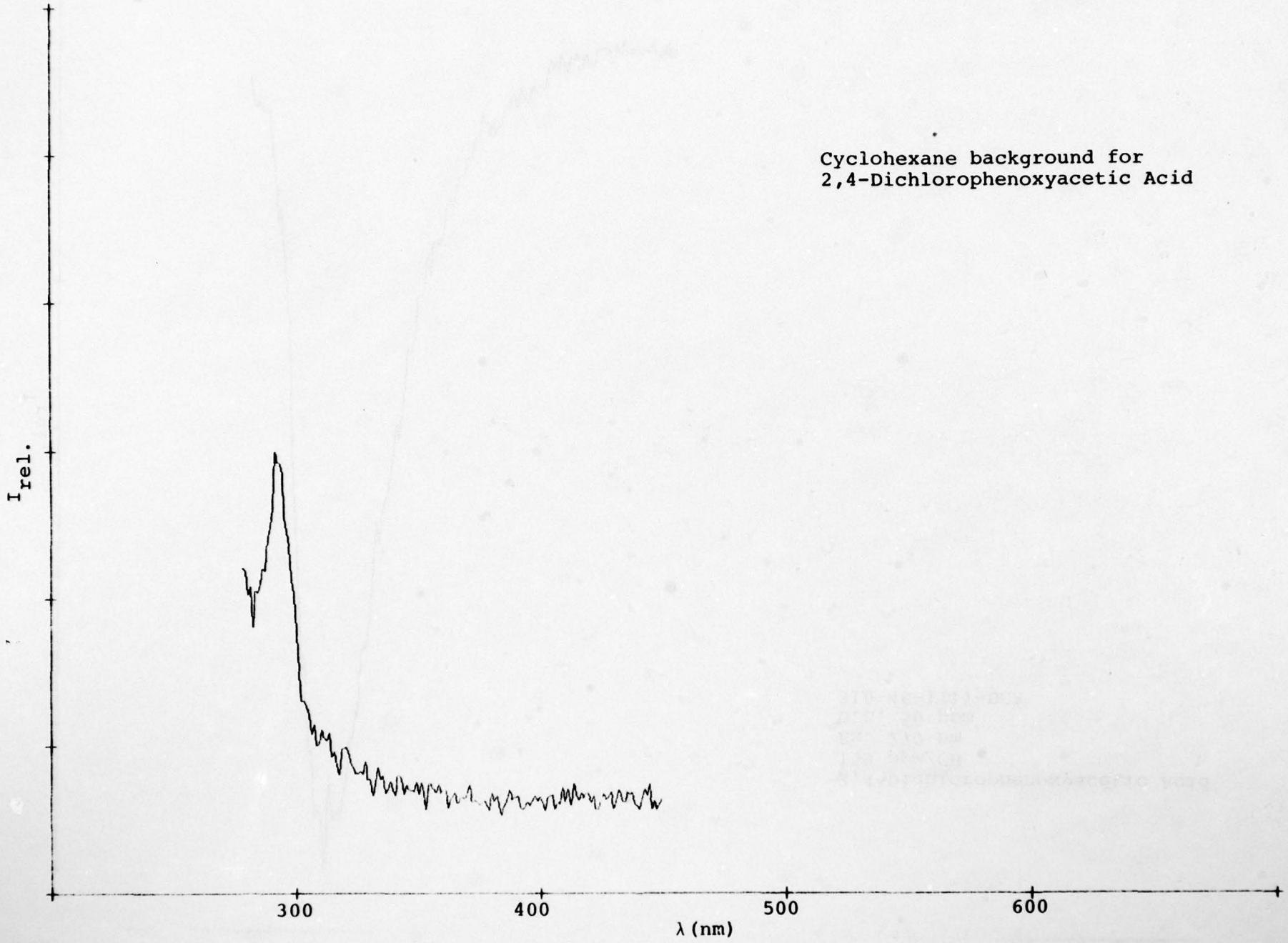
Cyclohexane background for Dichlone

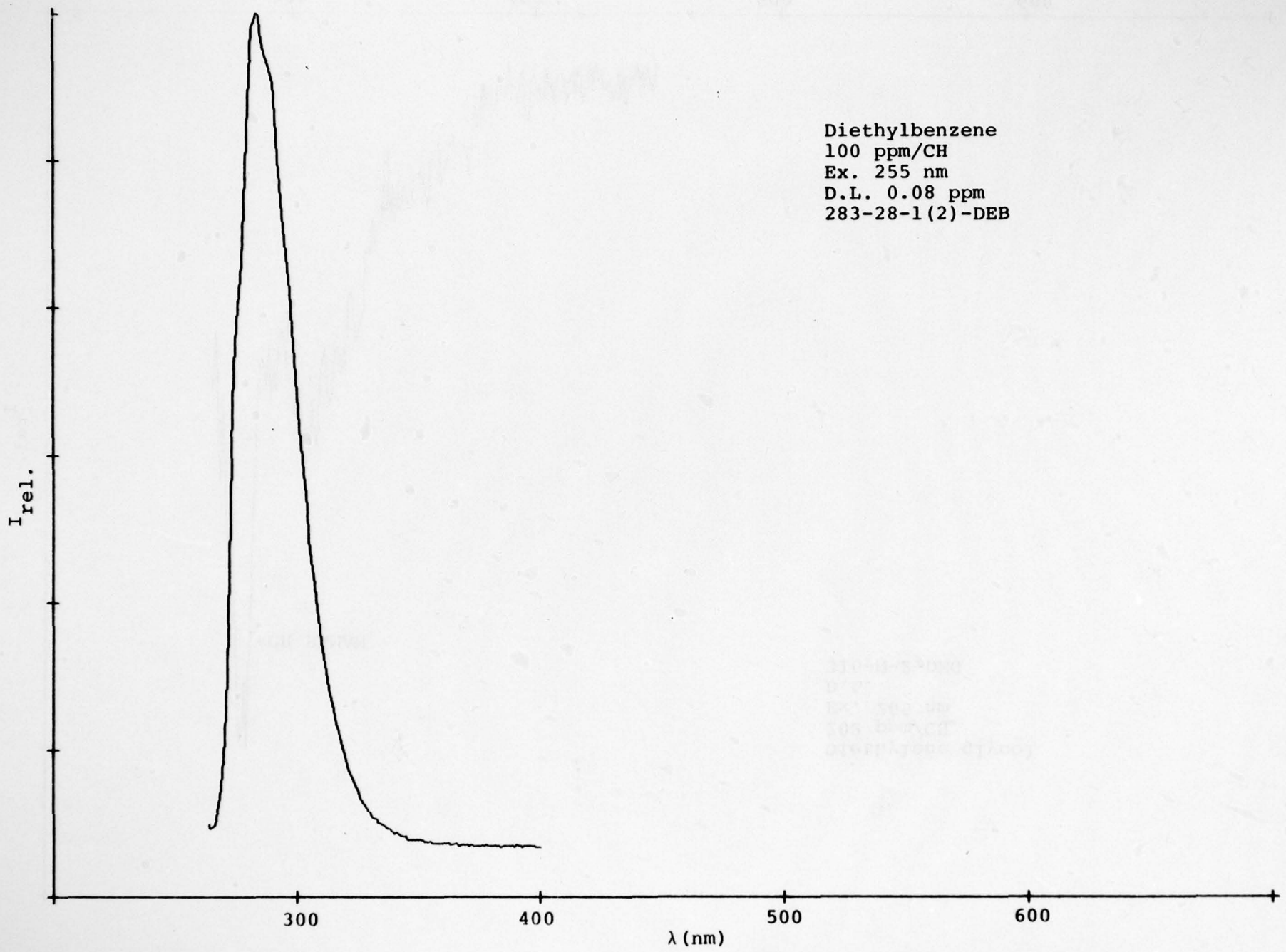

Dichlorobenil
110 ppm/CH
Ex. 285 nm
D.L. 0.6 ppm
312-30-1(2)-DIB
$I_{rel.}$
300
400
500
600
λ (nm)

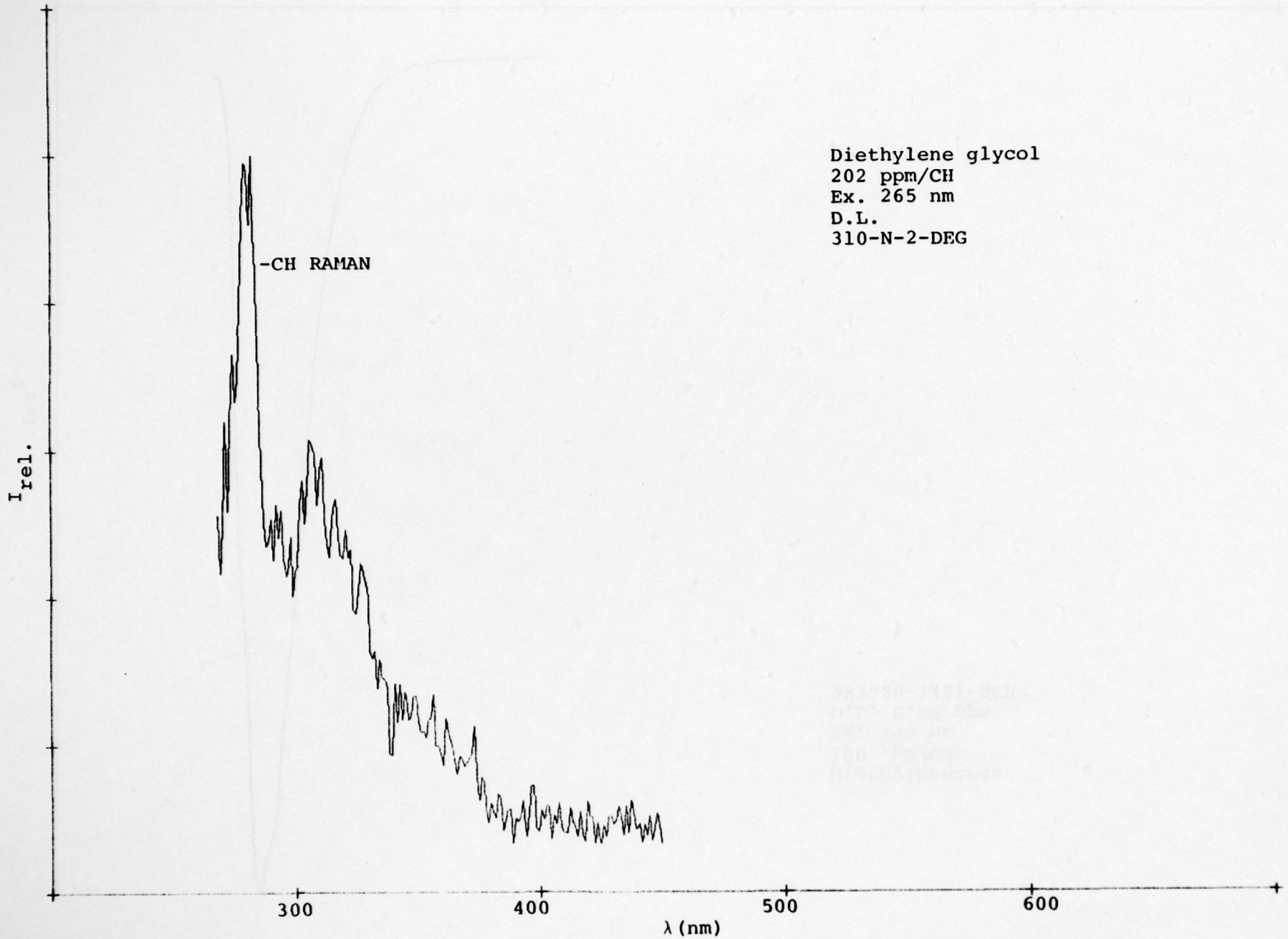

Dichlorodiphenyl silane
157 ppm/CH
Ex. 260 nm
D.L. 2 ppm
285-30-2(2)-DDS
I rel.
300
400
500
600
λ (nm)

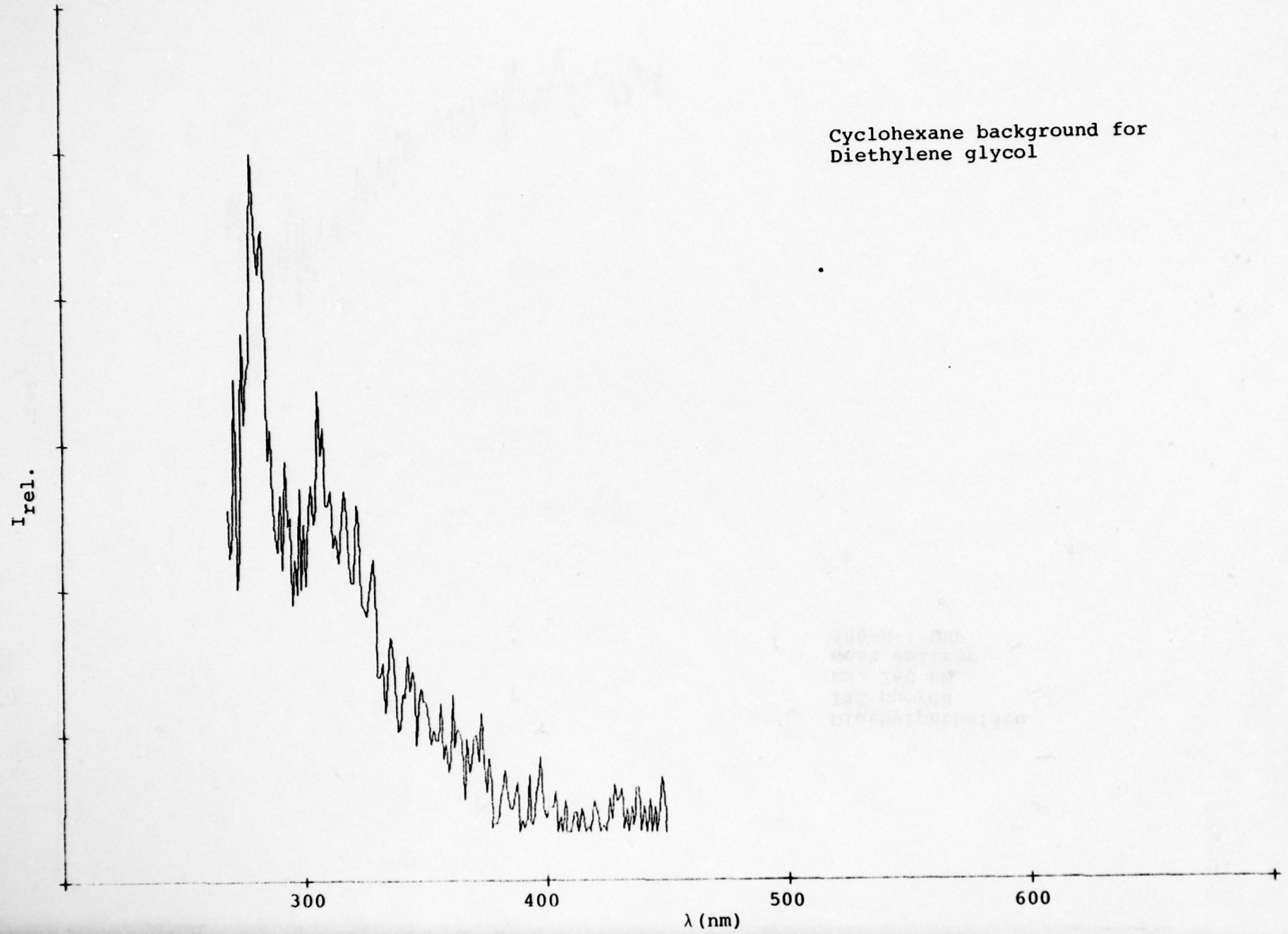

2,4-Dichlorophenoxyacetic Acid
159 ppm/CH
Ex. 270 nm
D.L. 30 ppm
310-46-1(1)-DCA
I rel.
300
400
500
600
λ (nm)

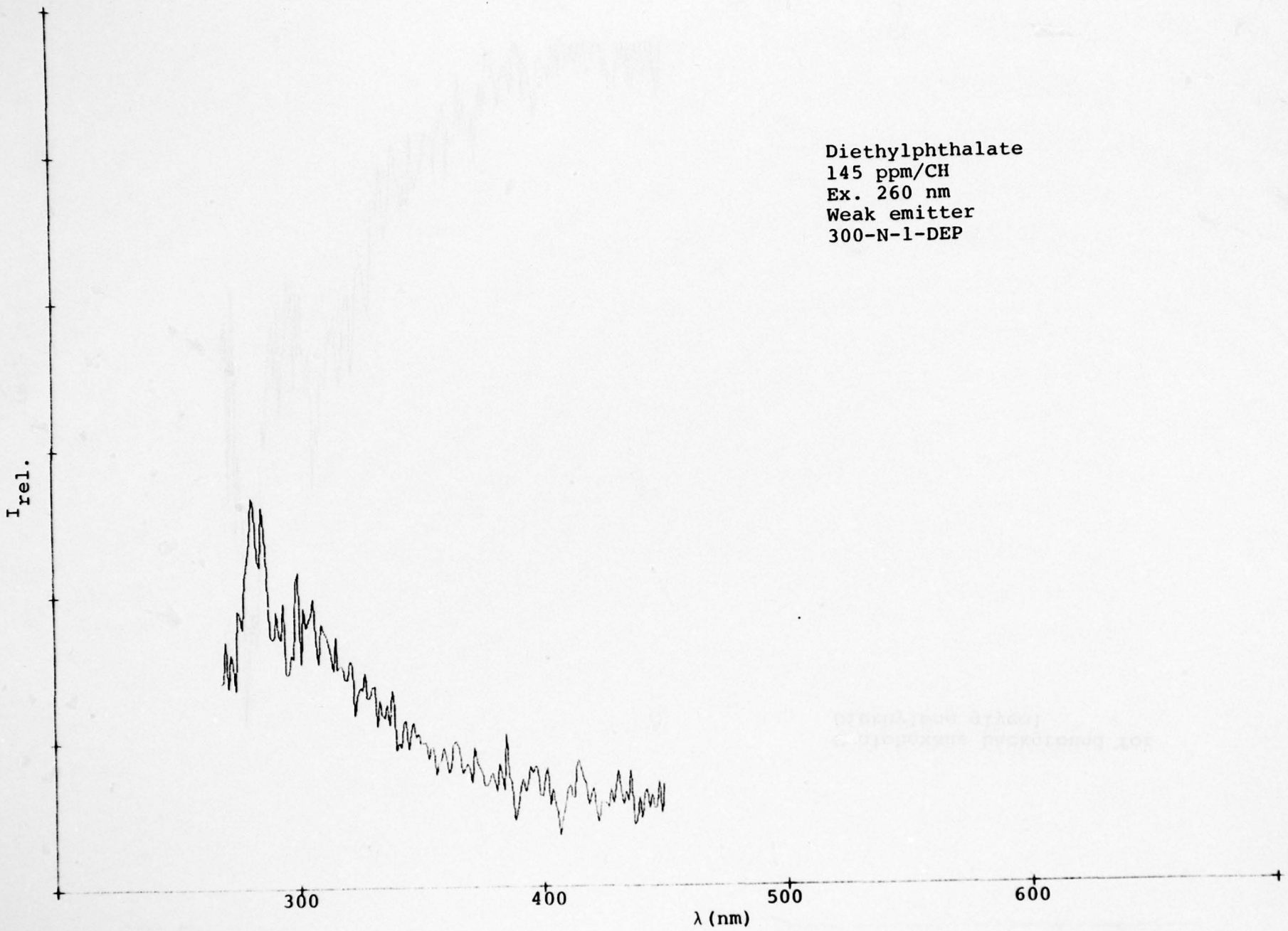
Cyclohexane background for
2,4-Dichlorophenoxyacetic Acid

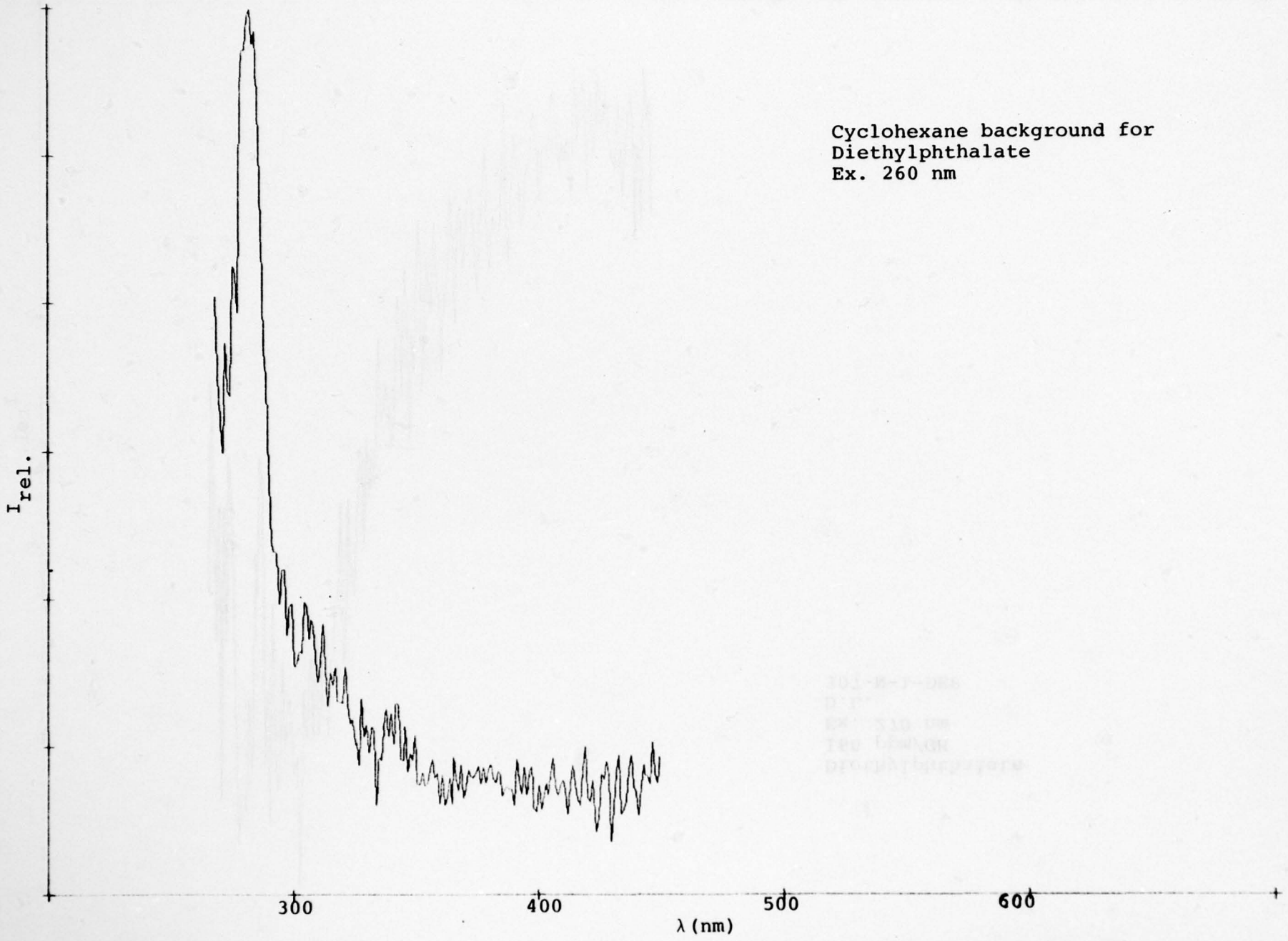



Diethylbenzene
100 ppm/CH
Ex. 255 nm
D.L. 0.08 ppm
283-28-1(2)-DEB
$I_{rel.}$
300
400
500
600
λ (nm)

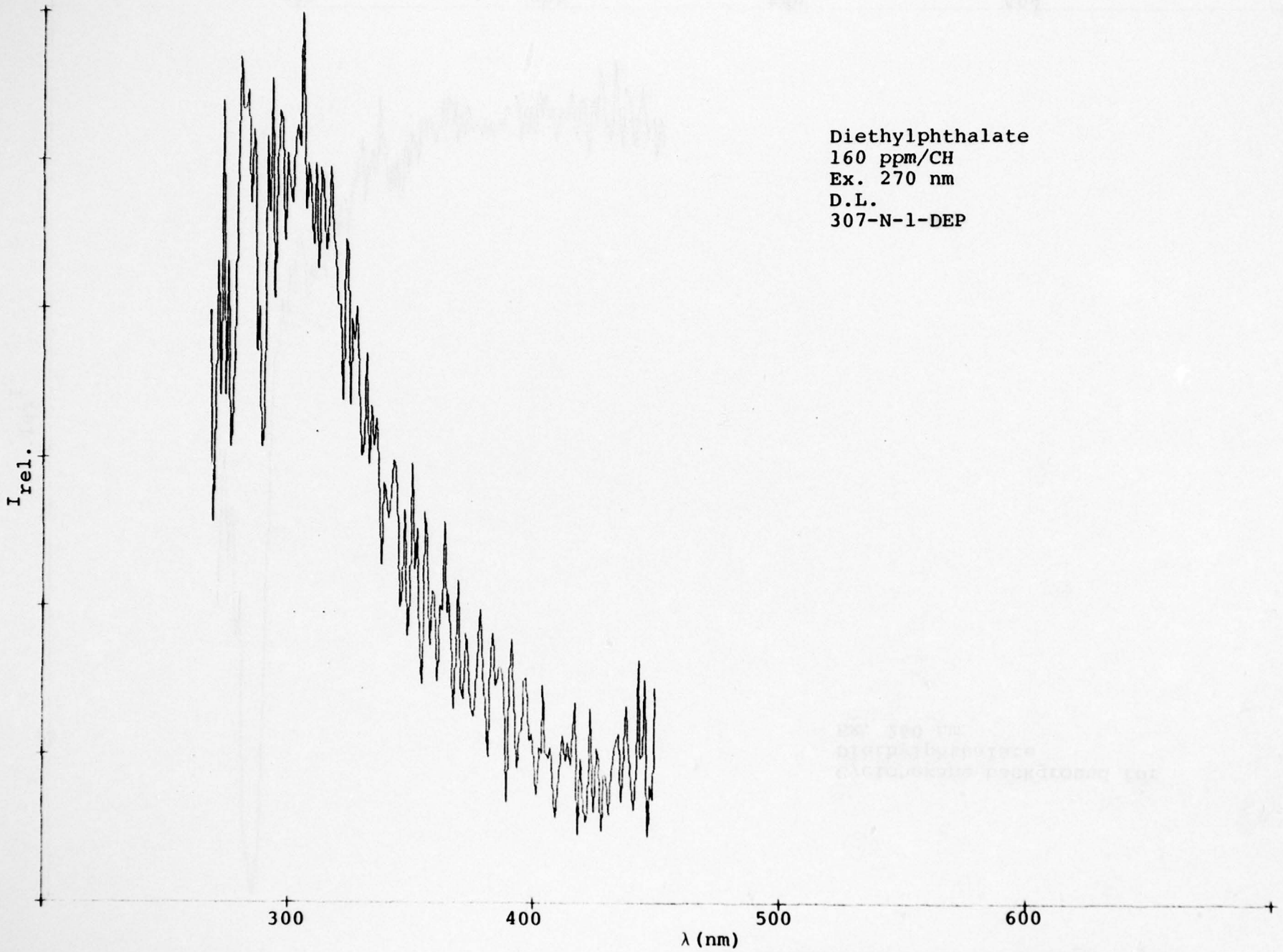

Diethylene glycol
202 ppm/CH
Ex. 265 nm
D.L.
310-N-2-DEG
-CH RAMAN
$I_{rel.}$
300
400
500
600
λ (nm)

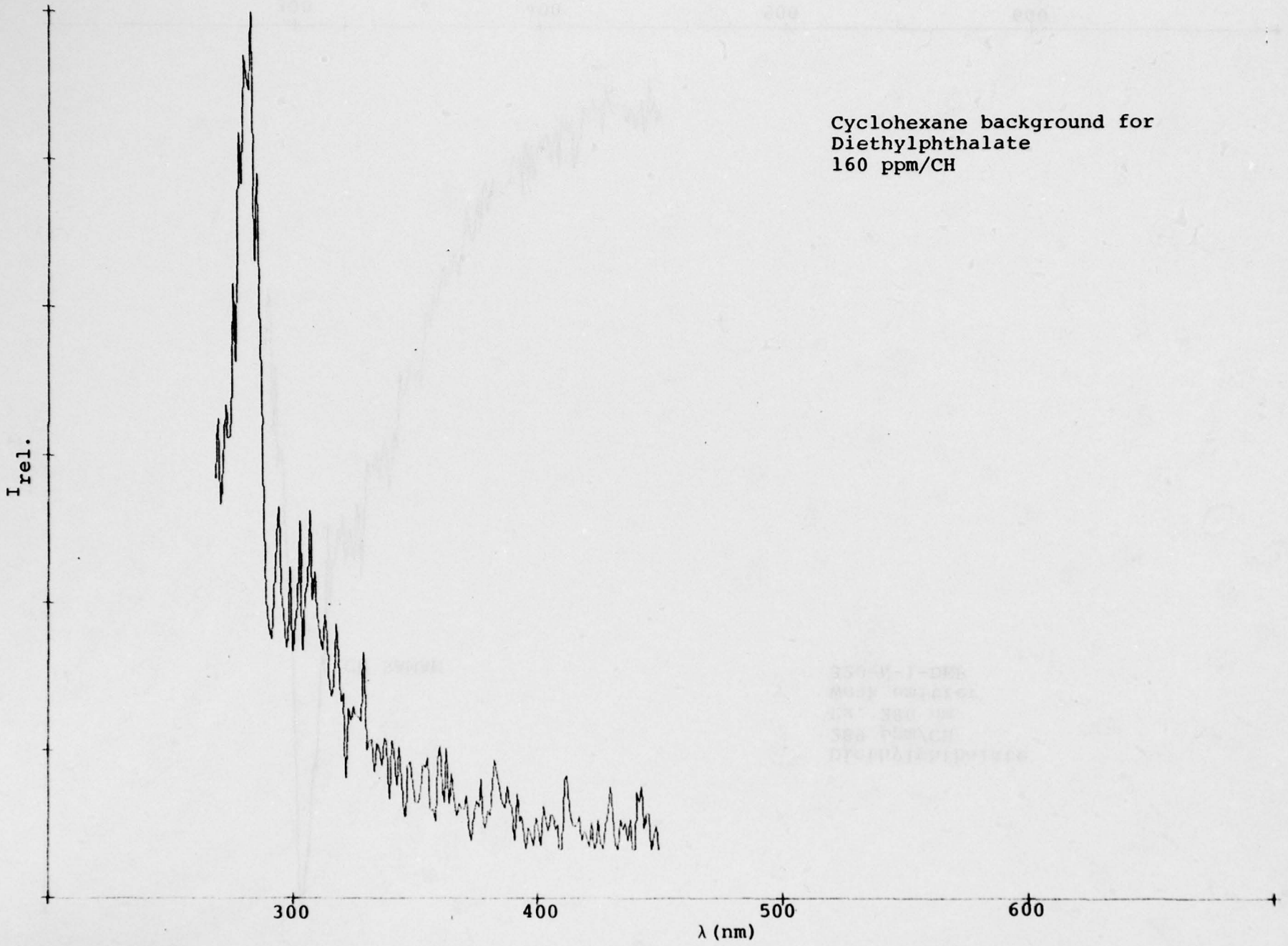

Cyclohexane background for
Diethylene glycol
$I_{rel.}$
300
400
500
600
λ (nm)

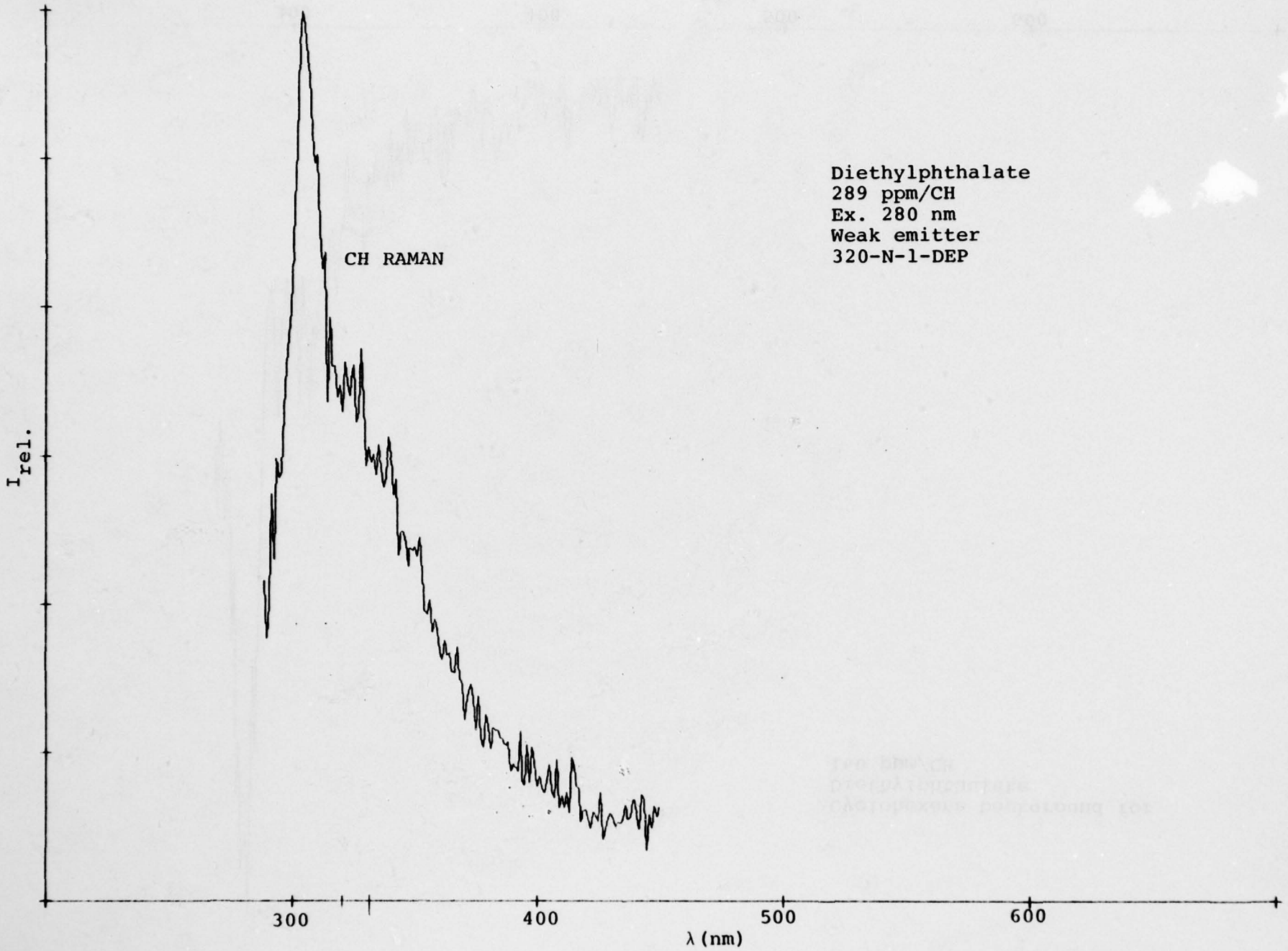

Diethylphthalate
145 ppm/CH
Ex. 260 nm
Weak emitter
300-N-1-DEP
$I_{rel.}$
300
400
500
600
λ (nm)

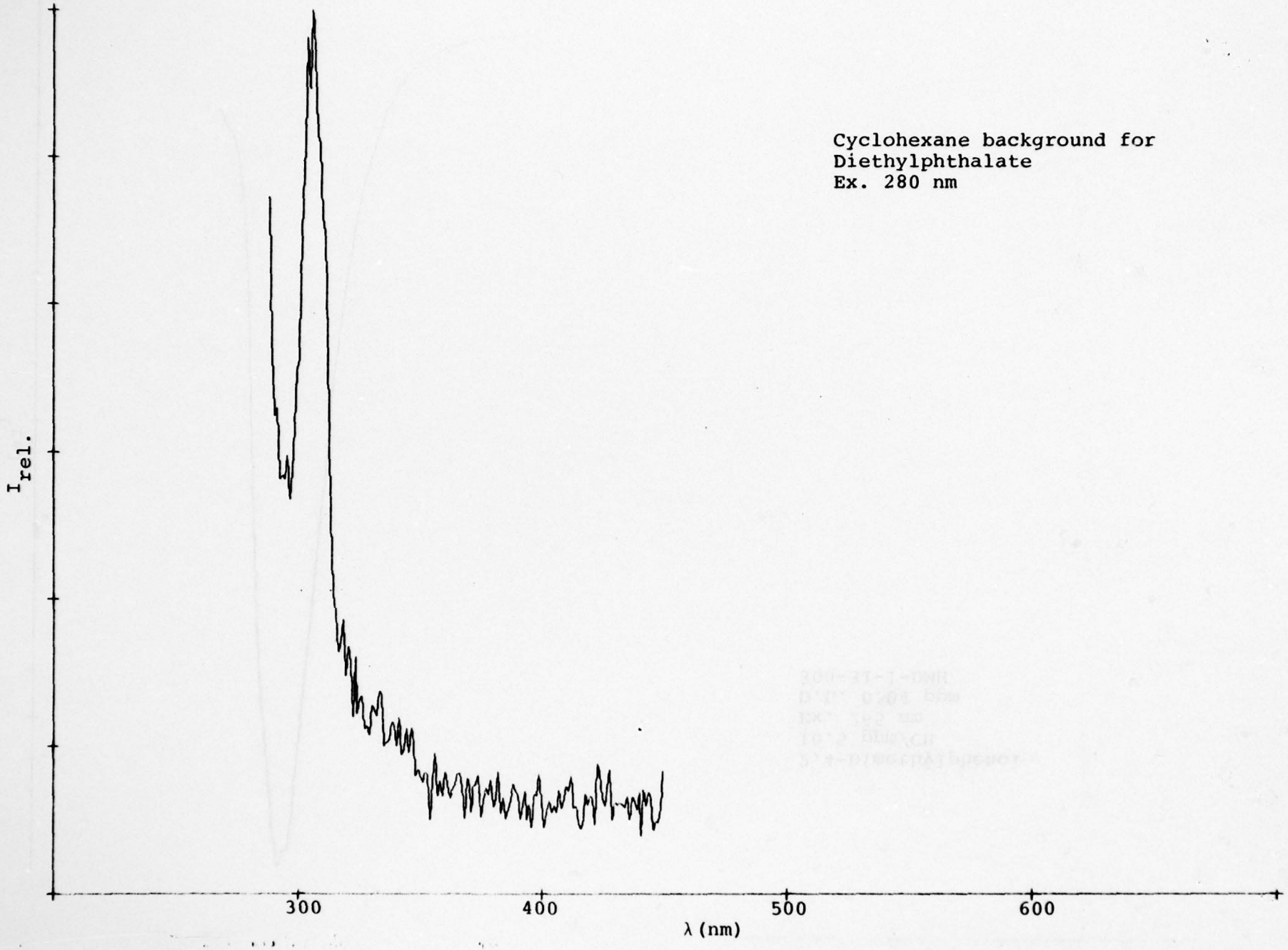


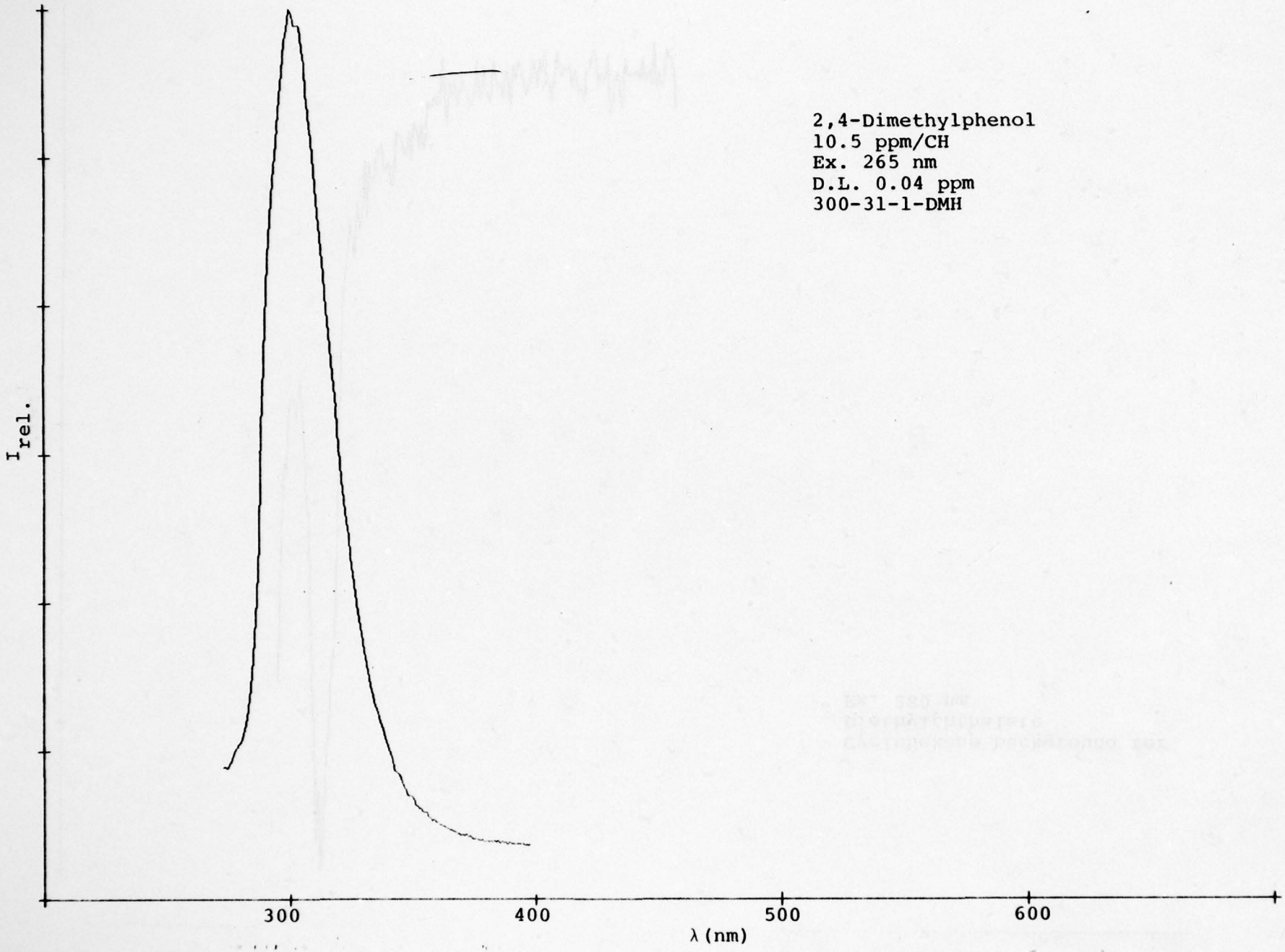
Cyclohexane background for
Diethylphthalate
Ex. 260 nm

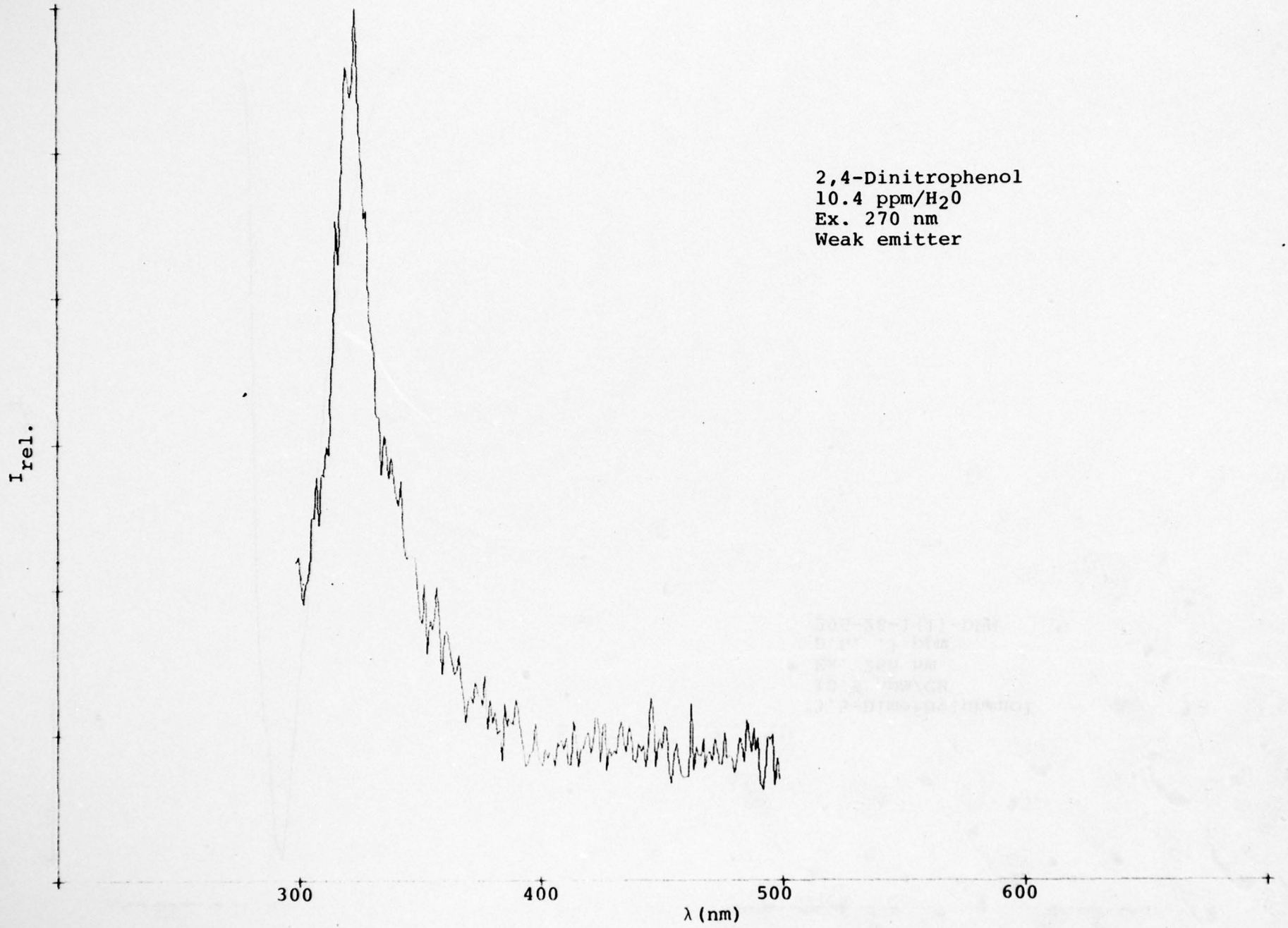

Diethylphthalate
160 ppm/CH
Ex. 270 nm
D.L.
307-N-1-DEP
$I_{rel.}$
300
400
500
600
λ (nm)

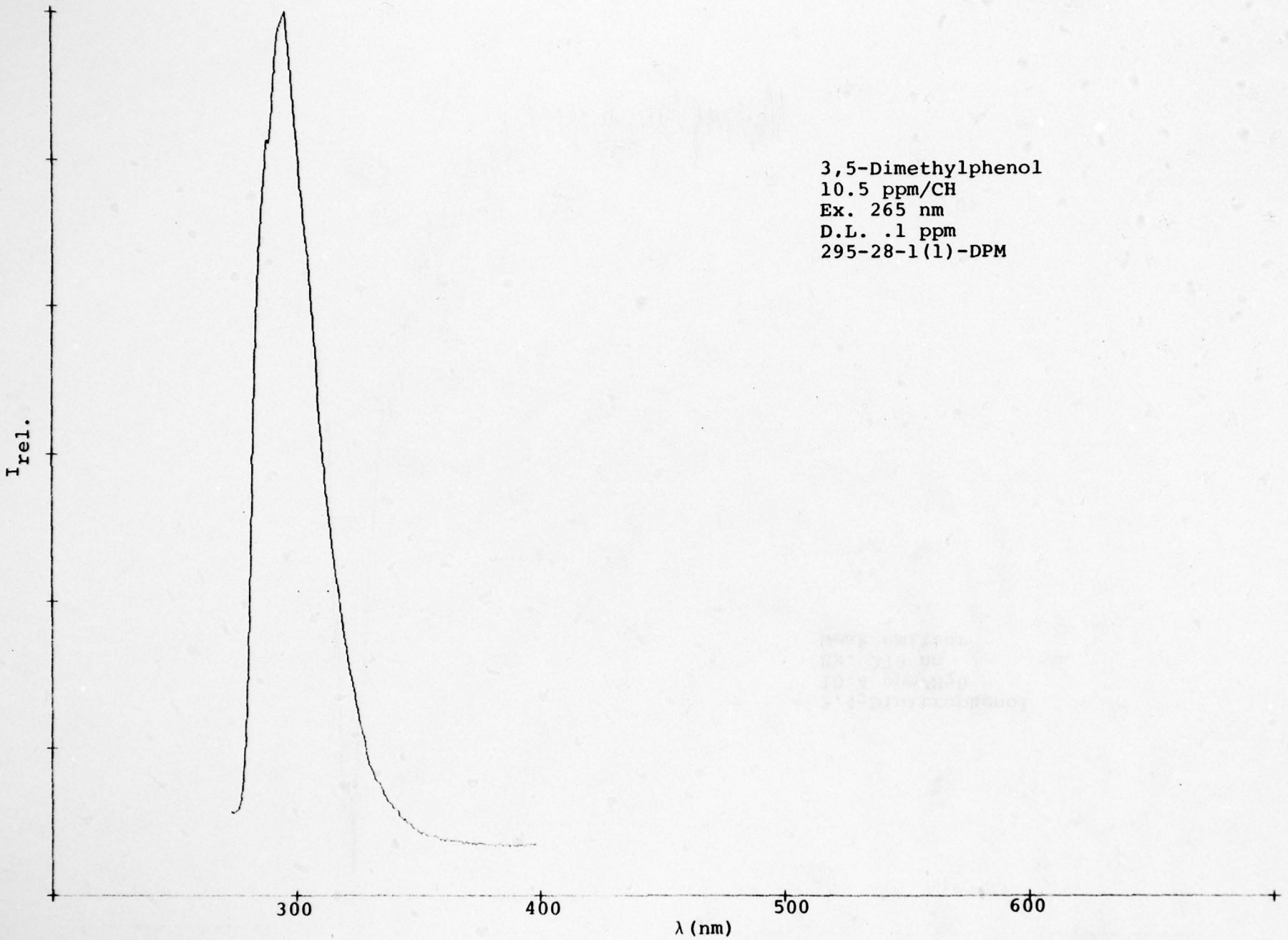

Cyclohexane background for
Diethylphthalate
160 ppm/CH
$I_{rel.}$
300
400
500
600
λ (nm)


Diethylphthalate
289 ppm/CH
Ex. 280 nm
Weak emitter
320-N-1-DEP
CH RAMAN
$I_{rel.}$
300
400
500
600
λ (nm)

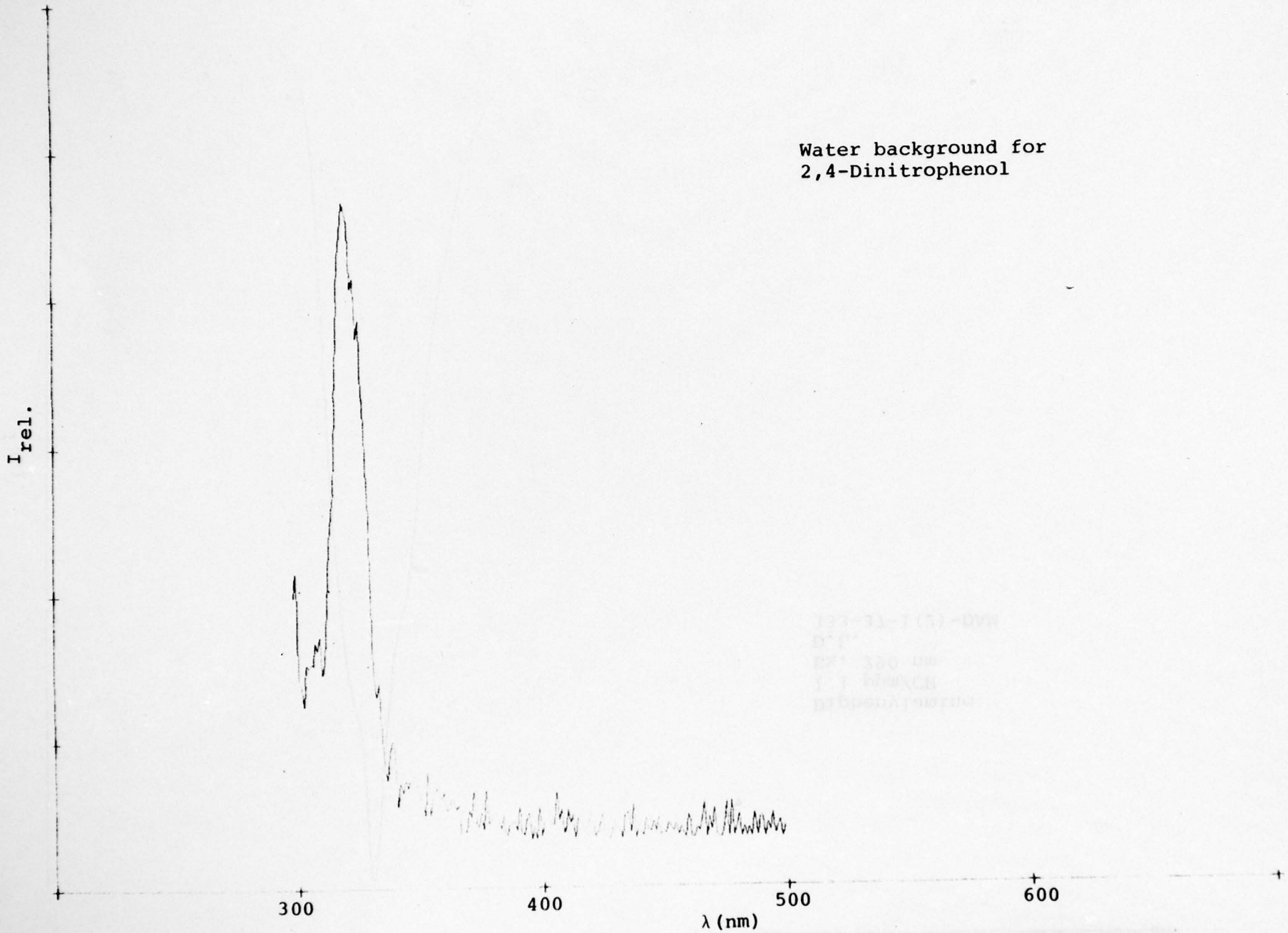

Cyclohexane background for
Diethylphthalate
Ex. 280 nm
$I_{rel.}$
300
400
500
600
λ (nm)

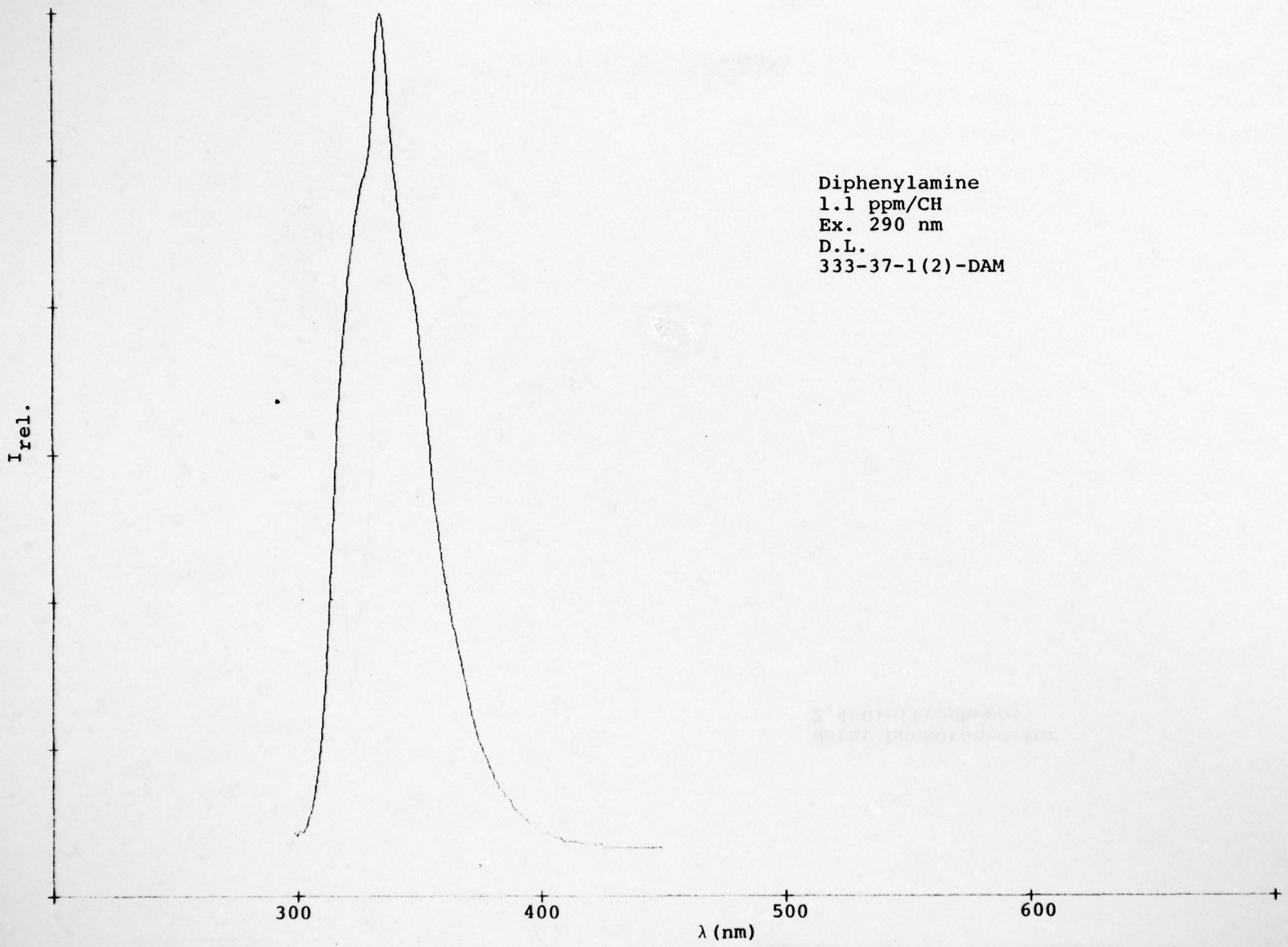

2,4-Dimethylphenol
10.5 ppm/CH
Ex. 265 nm
D.L. 0.04 ppm
300-31-1-DMH
I rel.
300
400
500
600
λ (nm)


2,4-Dinitrophenol
10.4 ppm/H_2O
Ex. 270 nm
Weak emitter
$I_{rel.}$
300
400
500
600
λ (nm)


3,5-Dimethylphenol
10.5 ppm/CH
Ex. 265 nm
D.L. .1 ppm
295-28-1(1)-DPM
I rel.
300
400
500
600
λ (nm)

Water background for
2,4-Dinitrophenol

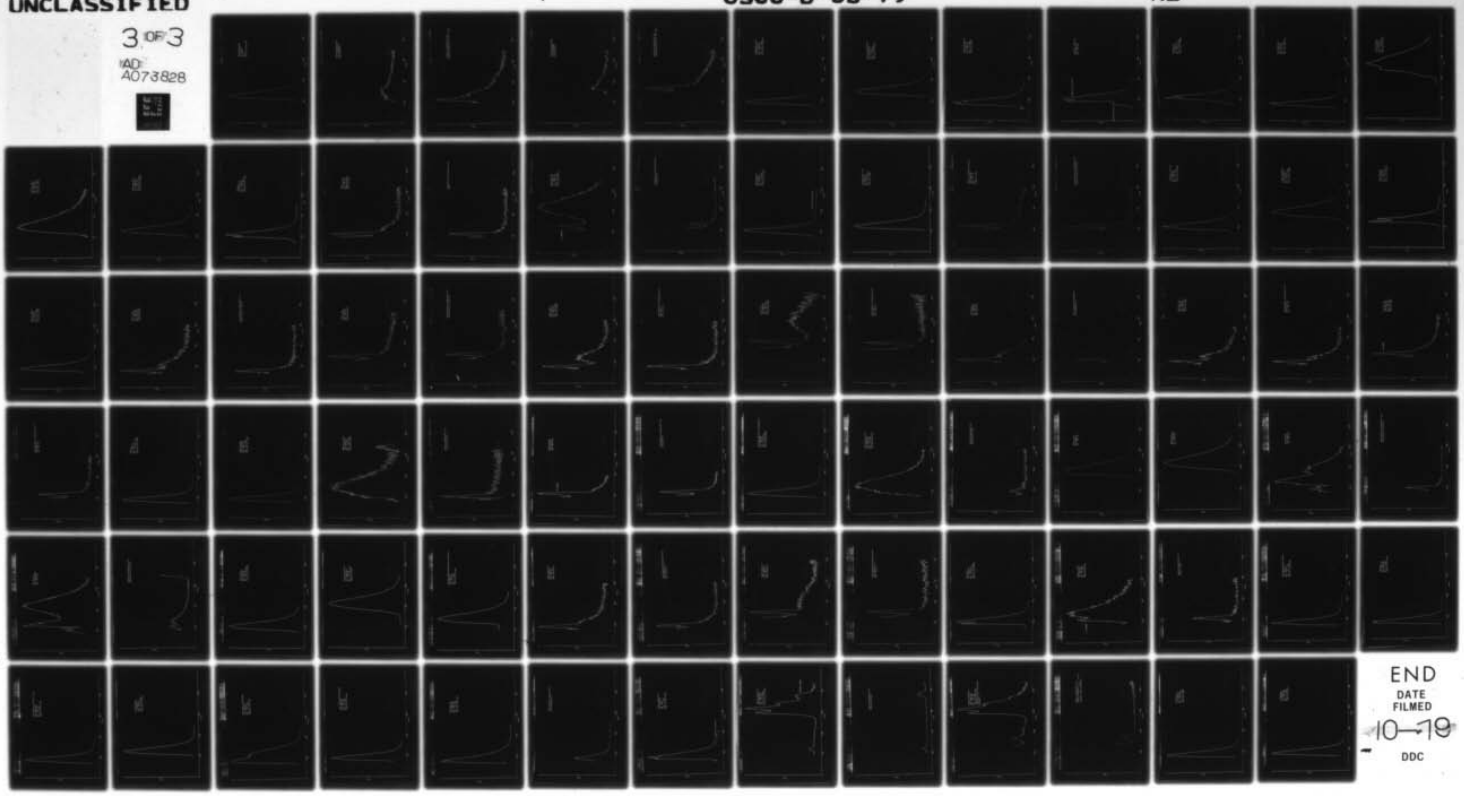



Diphenylamine
1.1 ppm/CH
Ex. 290 nm
D.L.
333-37-1(2)-DAM
$I_{rel.}$
300
400
500
600
λ (nm)

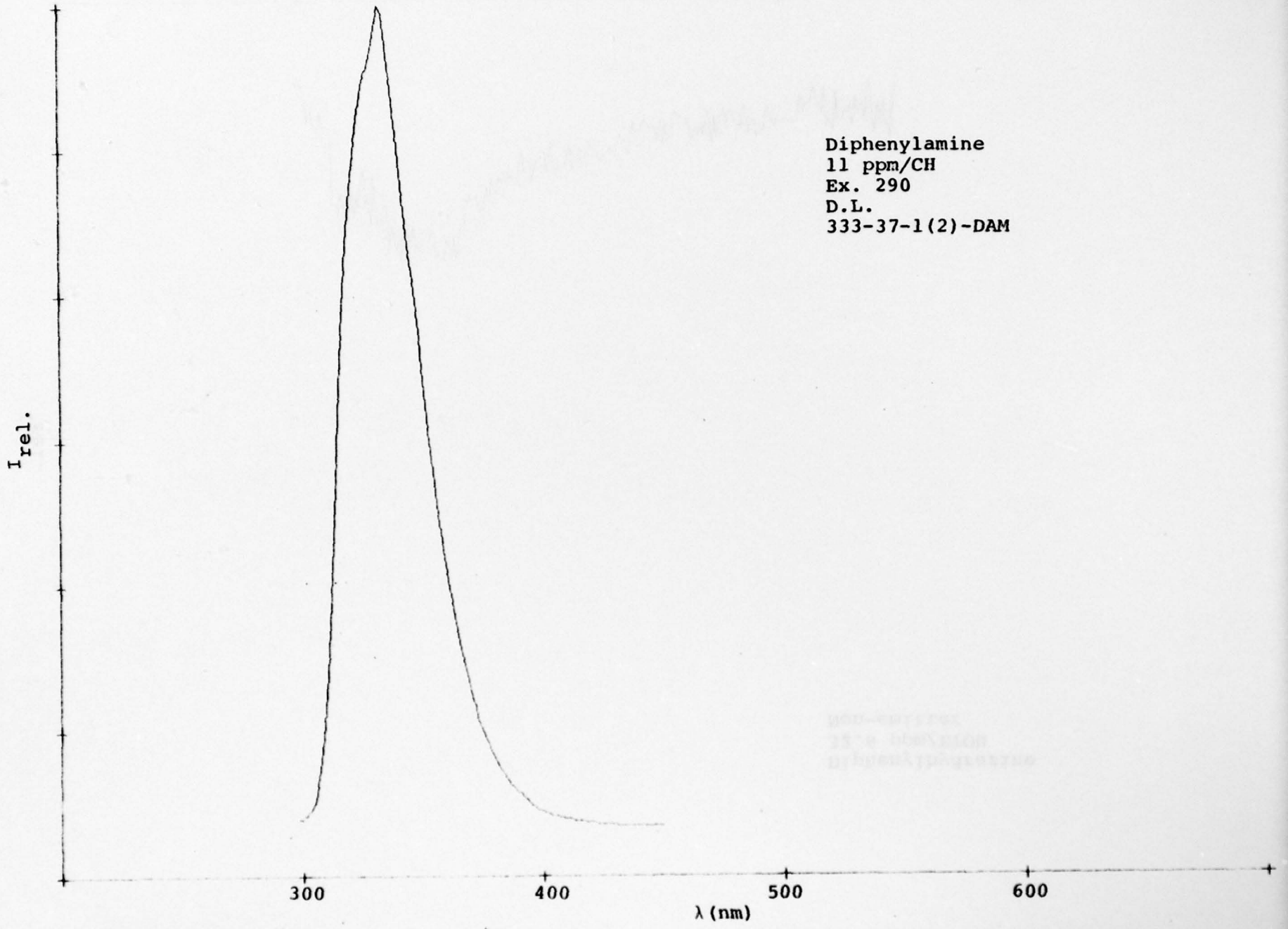
AD-A073 828 BAIRD CORP BEDFORD MA GOVERNMENT SYSTEMS DIV F/G 7/2
A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS,(U)
MAY 79 J T BROWNRIGG, D A BUSCH, L P GIERING DOT-CG-81-78-1888
USCG-D-53-79 NL

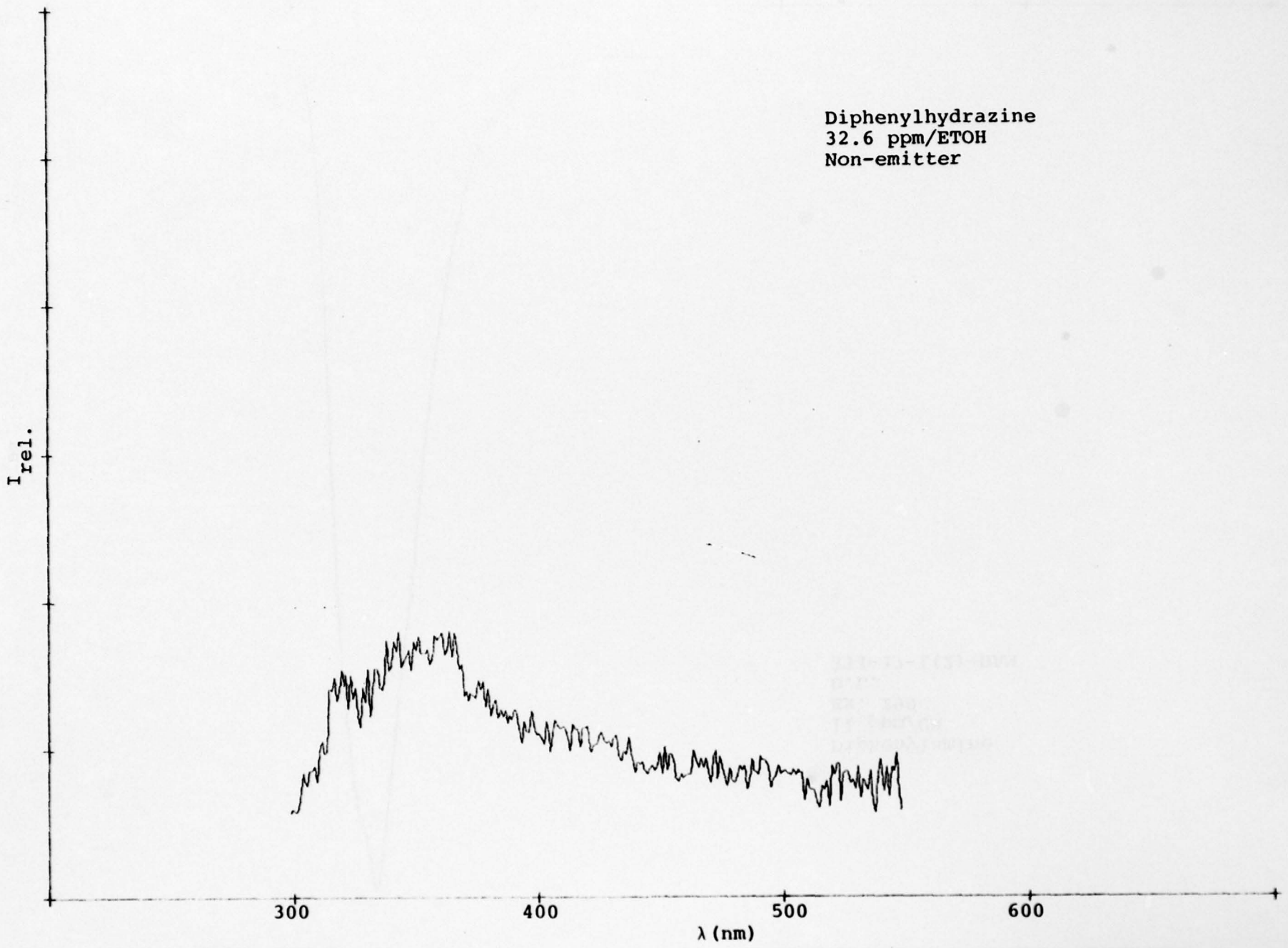
UNCLASSIFIED

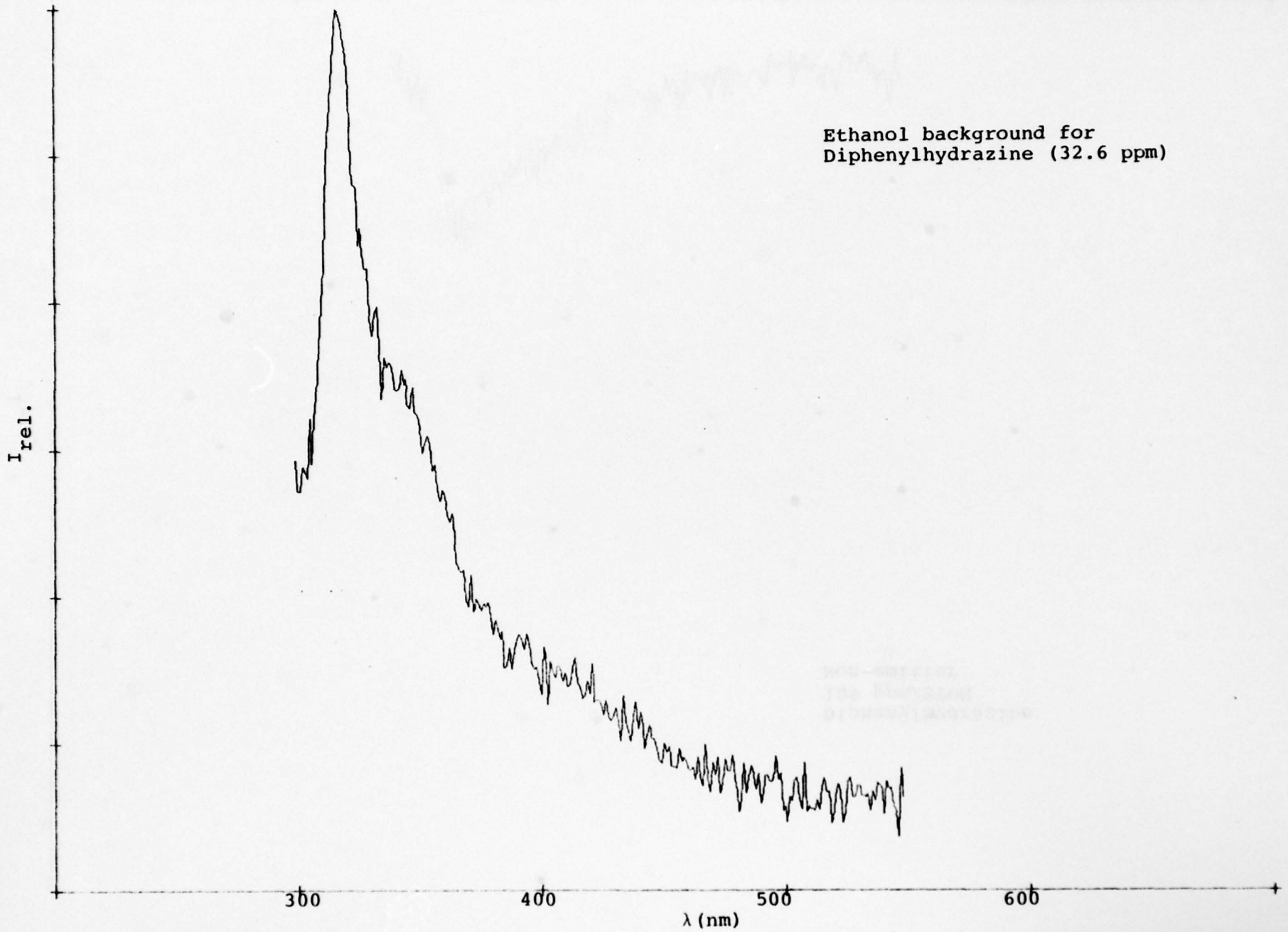
3 OF 3
AD A073828



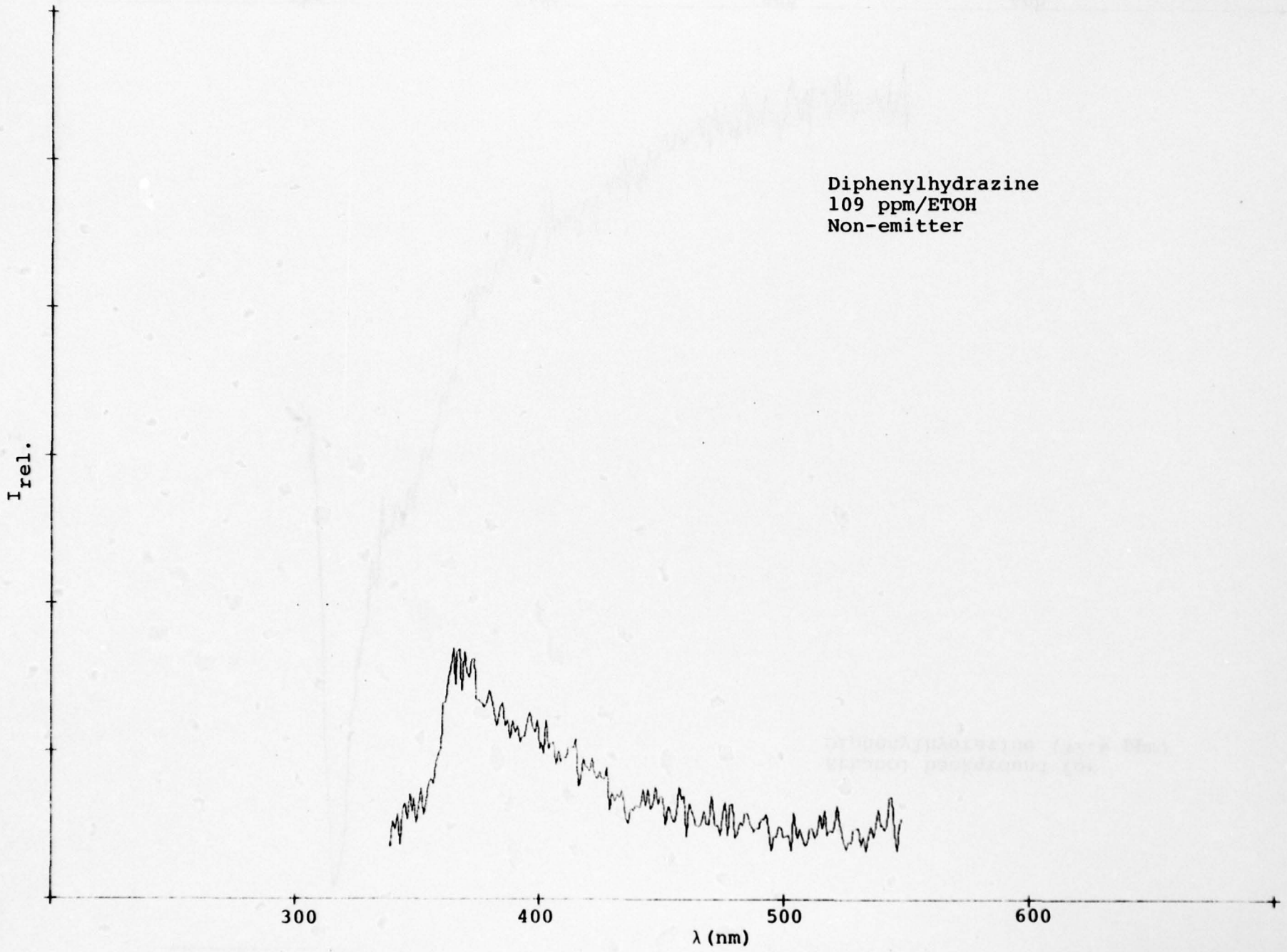
END
DATE FILMED
10-79
DDC

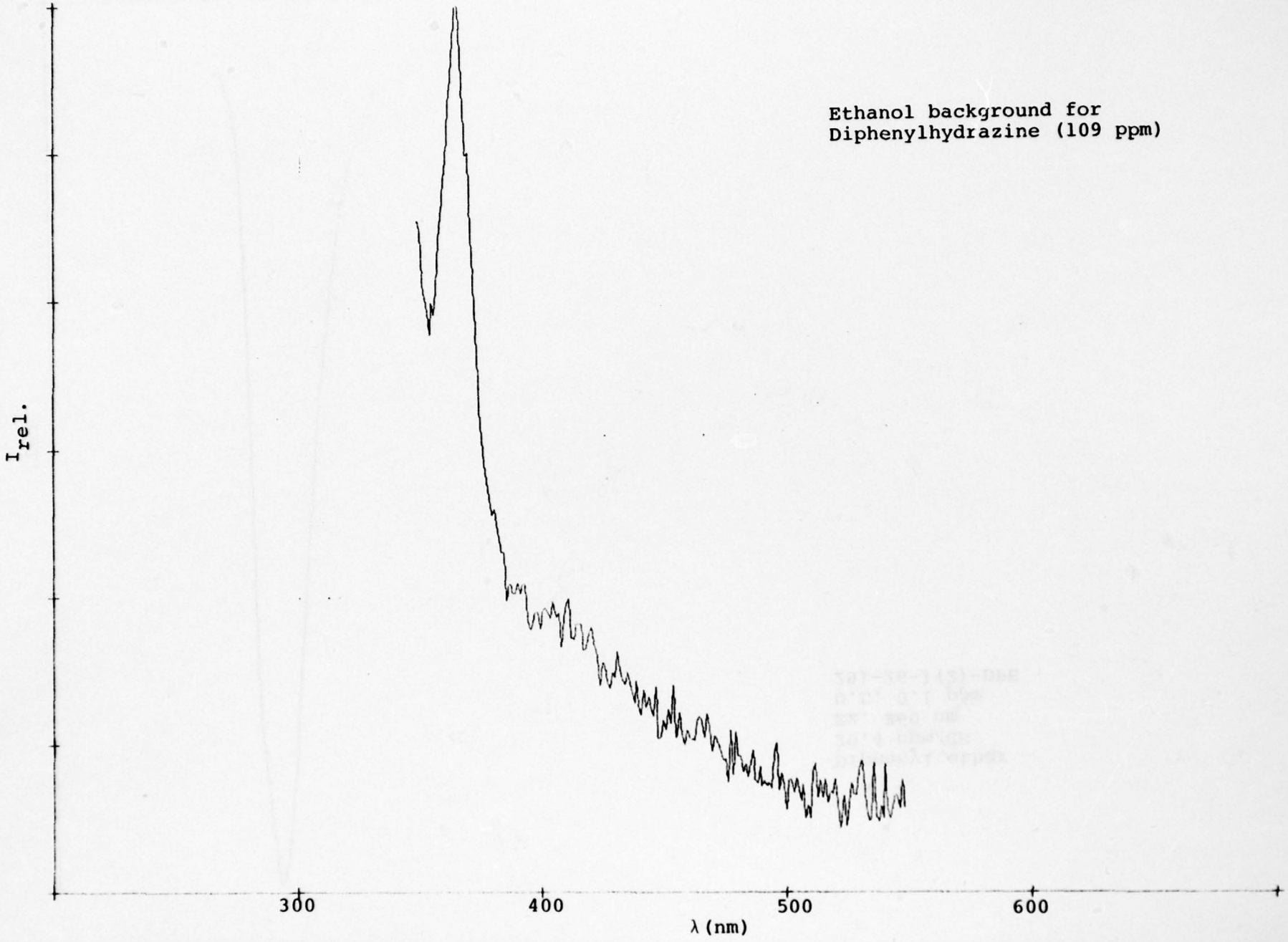

Diphenylamine
11 ppm/CH
Ex. 290
D.L.
333-37-1(2)-DAM
$I_{rel.}$
300
400
500
600
λ (nm)

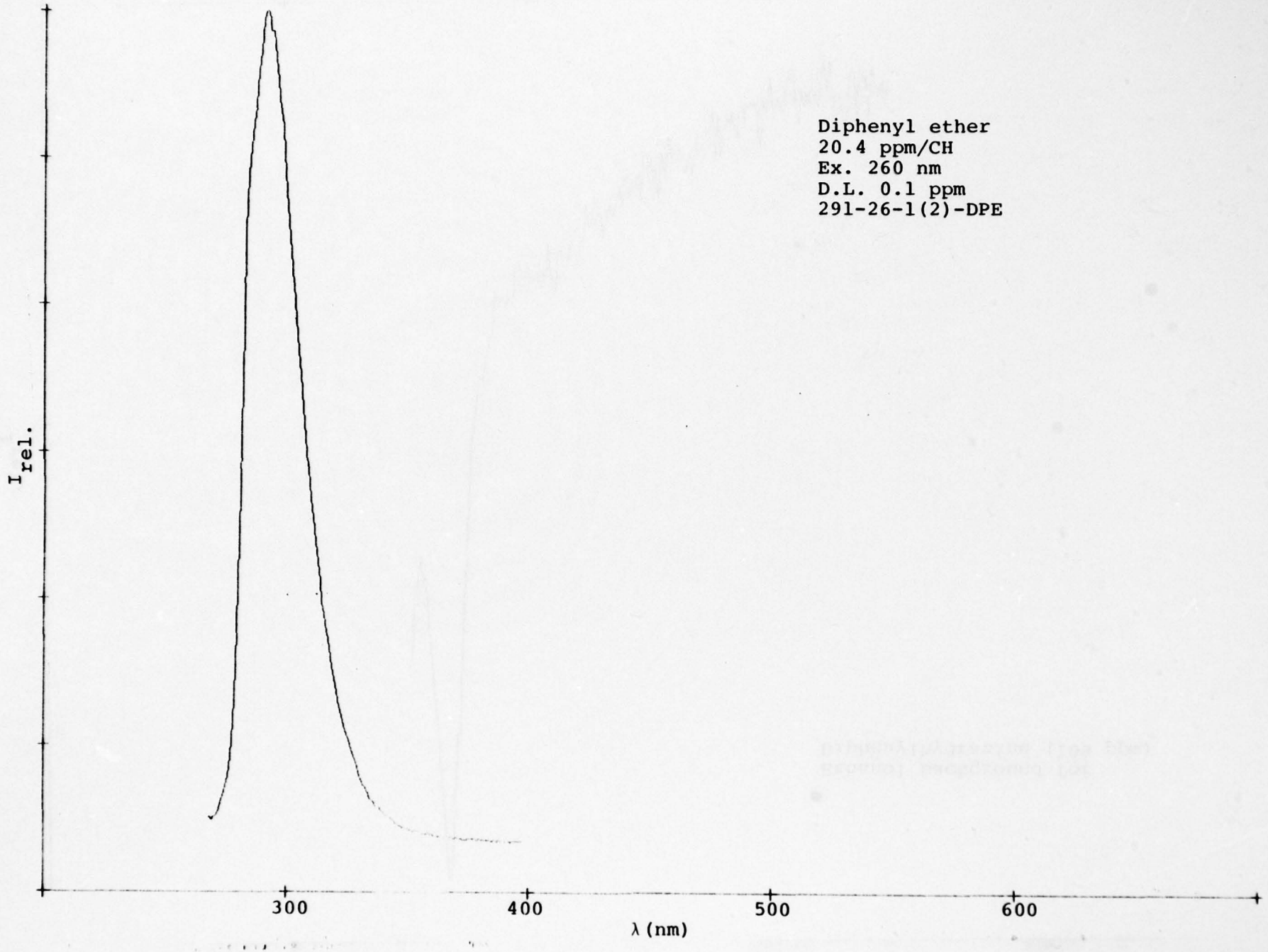

Diphenylhydrazine
32.6 ppm/ETOH
Non-emitter
$I_{rel.}$
300
400
500
600
λ (nm)

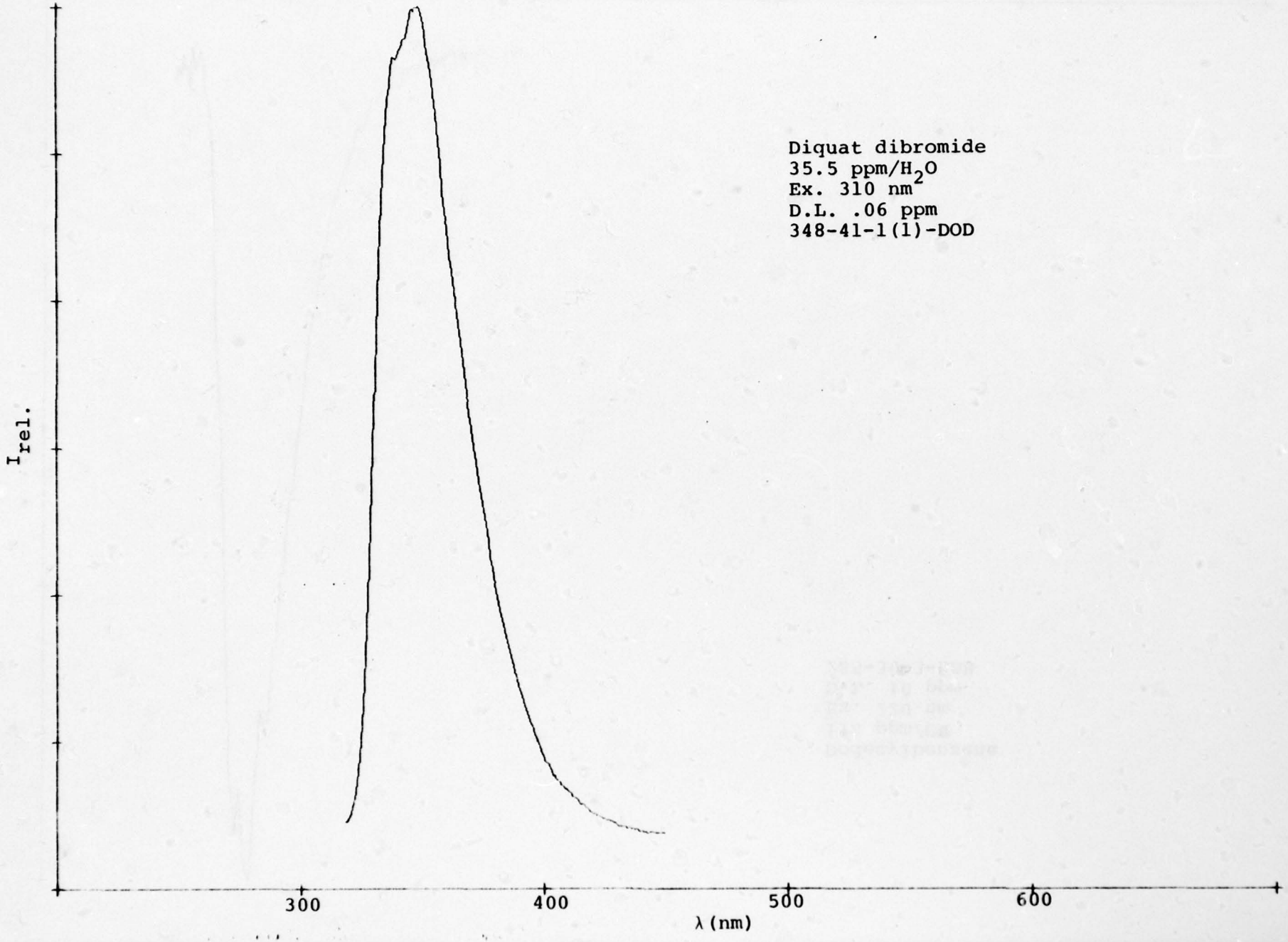

Ethanol background for
Diphenylhydrazine (32.6 ppm)
$I_{rel.}$
300
400
500
600
λ (nm)

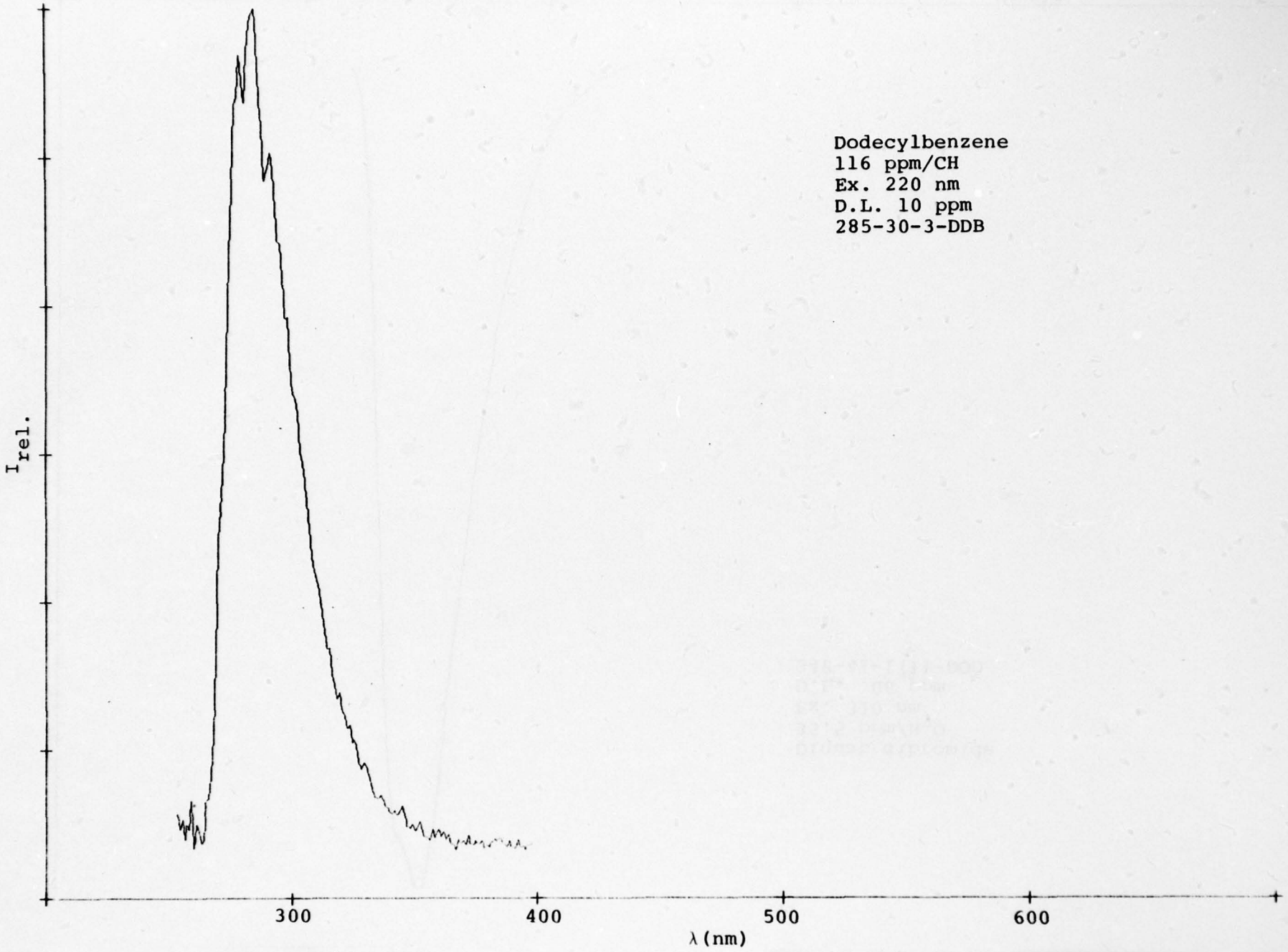
Diphenylhydrazine
109 ppm/ETOH
Non-emitter

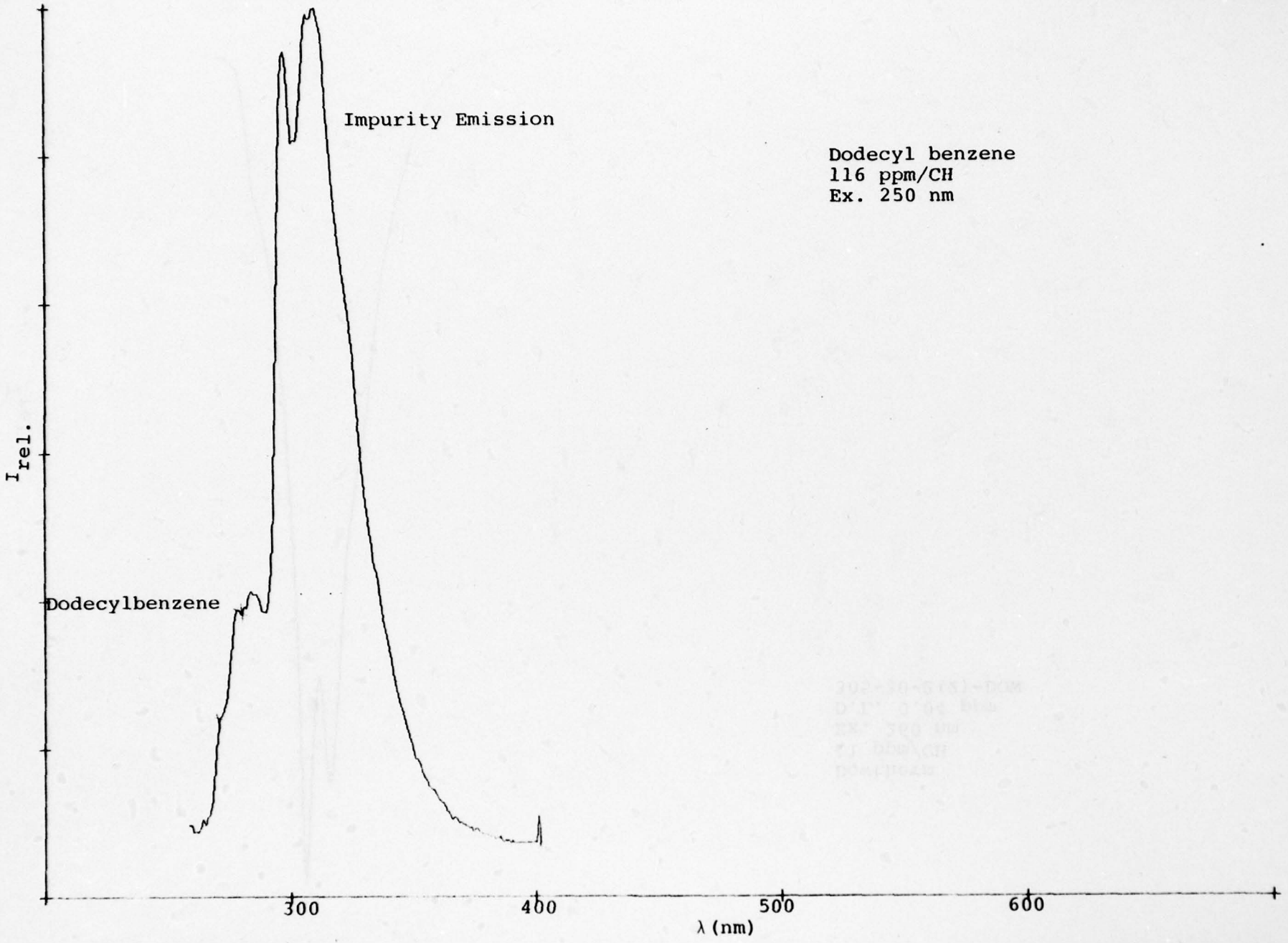


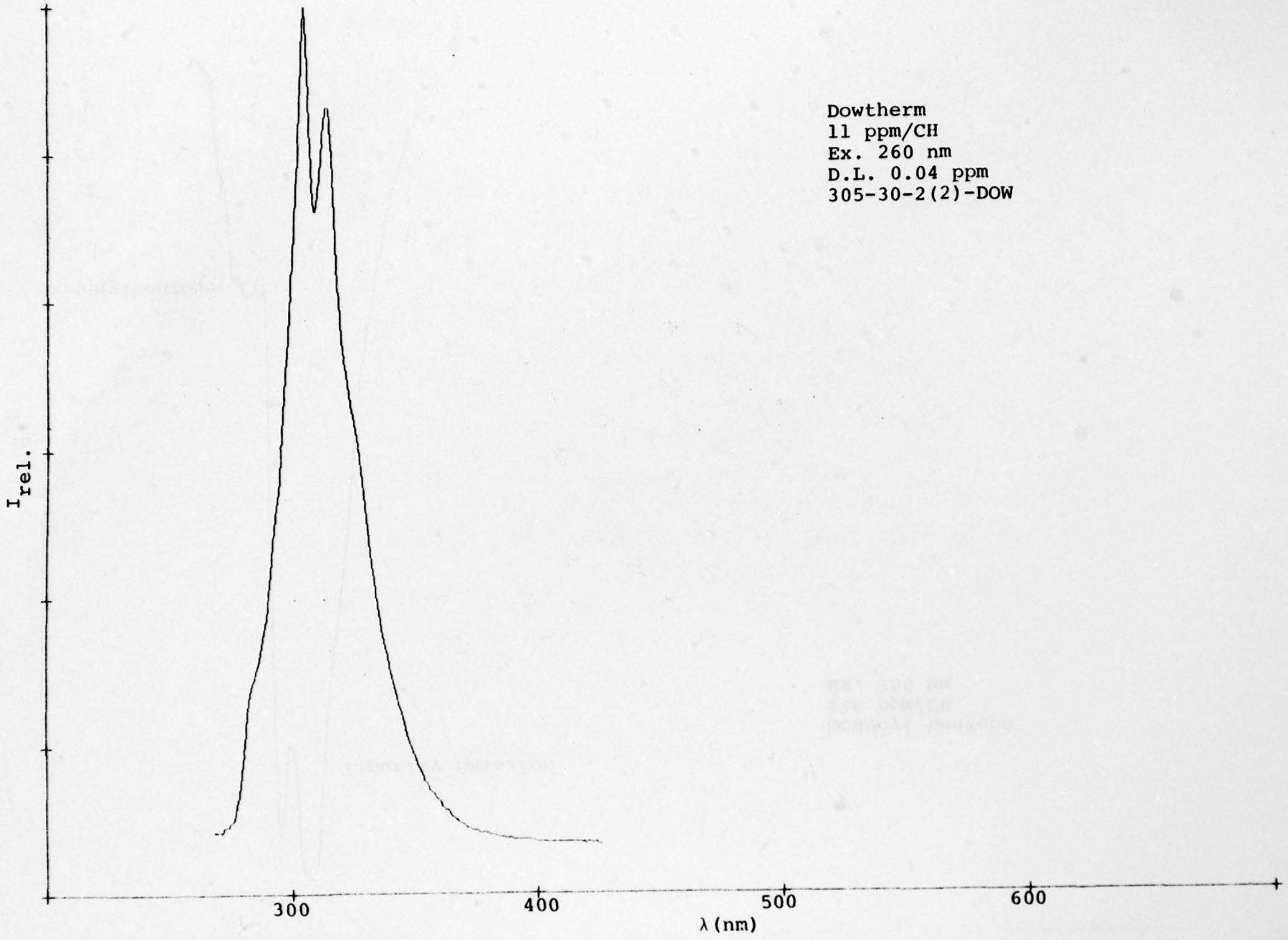

Ethanol background for
Diphenylhydrazine (109 ppm)
$I_{rel.}$
300
400
500
600
λ (nm)

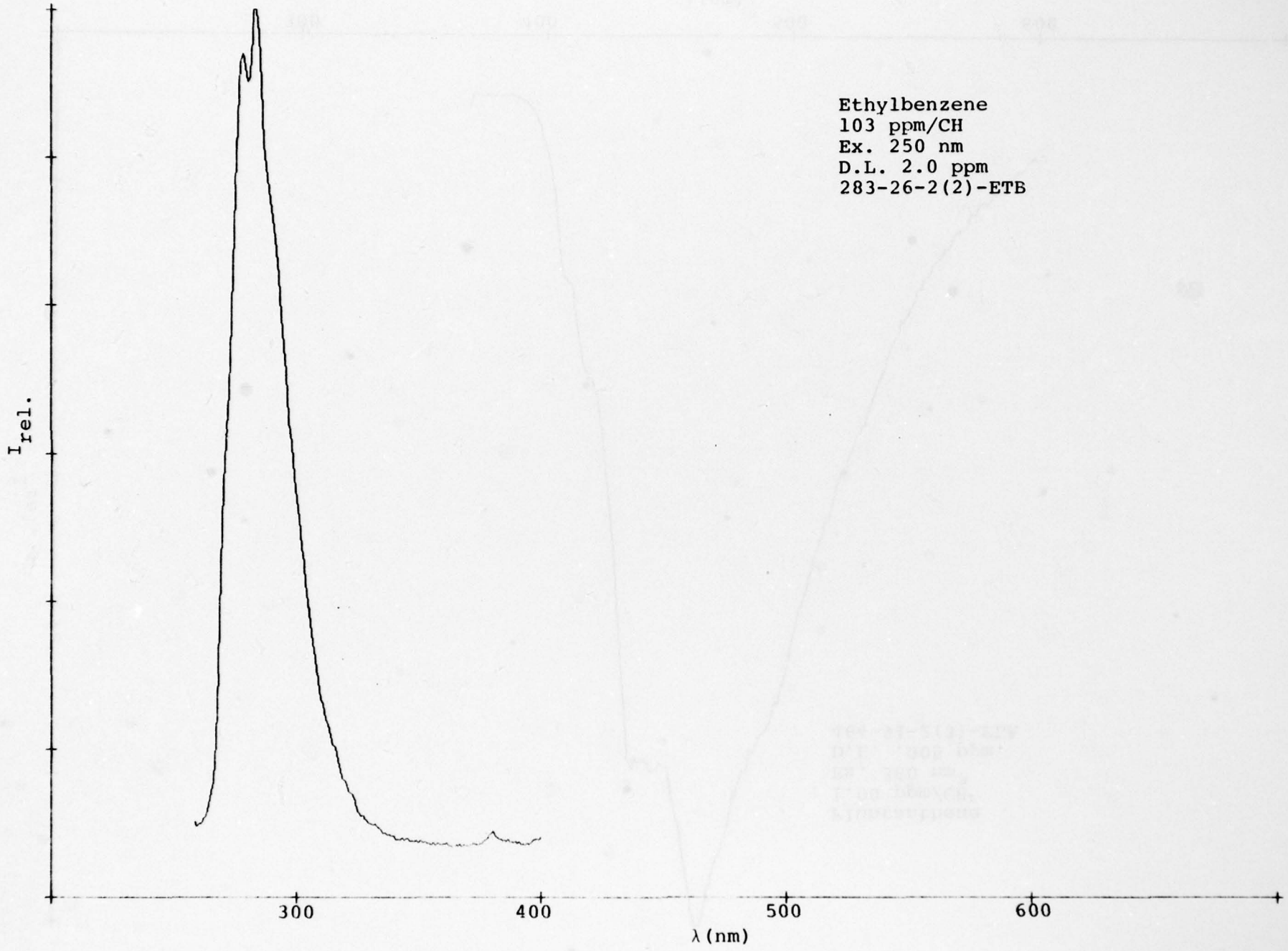

Diphenyl ether
20.4 ppm/CH
Ex. 260 nm
D.L. 0.1 ppm
291-26-1(2)-DPE
$I_{rel.}$
300
400
500
600
λ (nm)

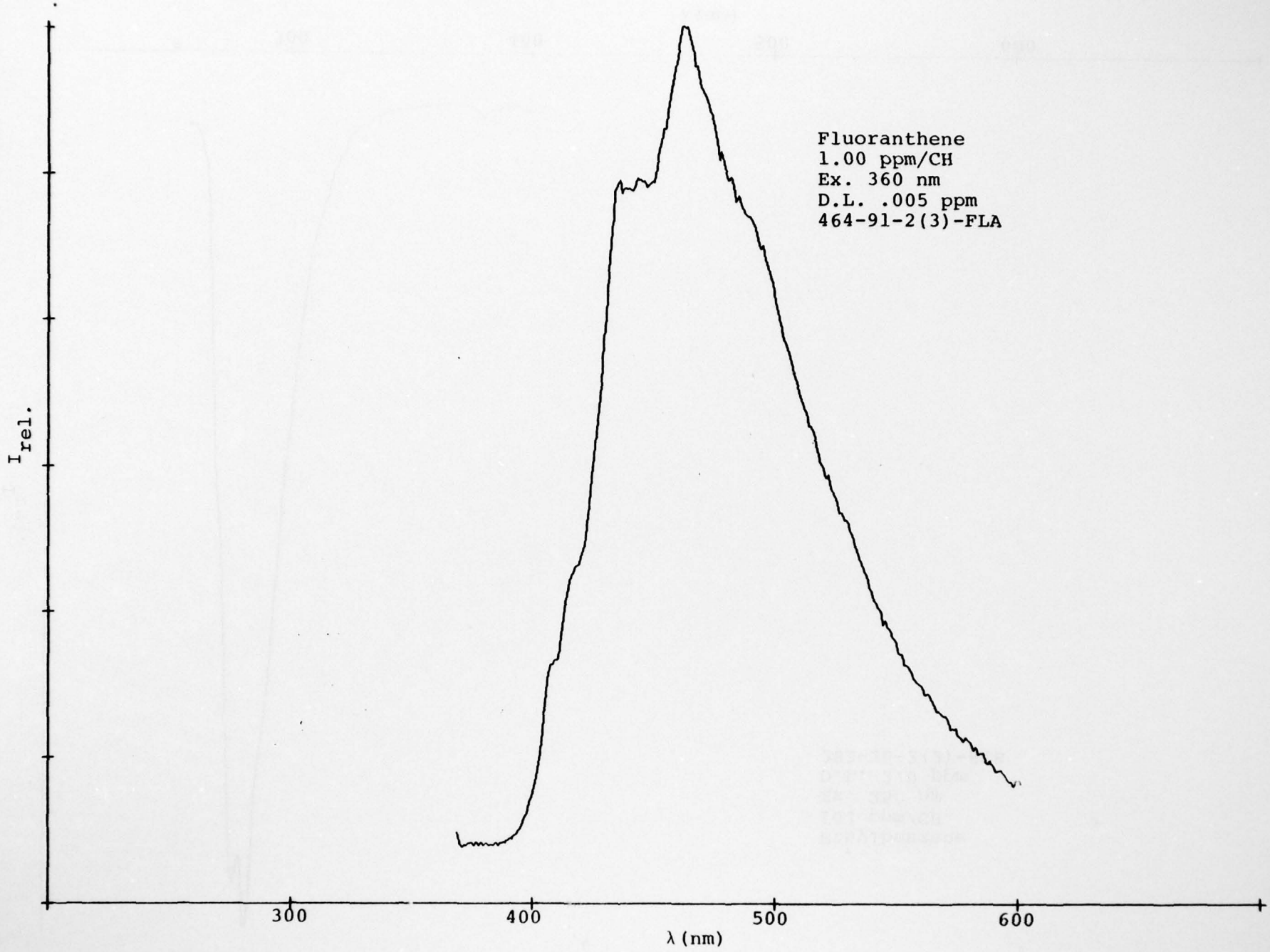

Diquat dibromide
35.5 ppm/H_2O
Ex. 310 nm
D.L. .06 ppm
348-41-1(1)-DOD
$I_{rel.}$
300
400
500
600
λ (nm)

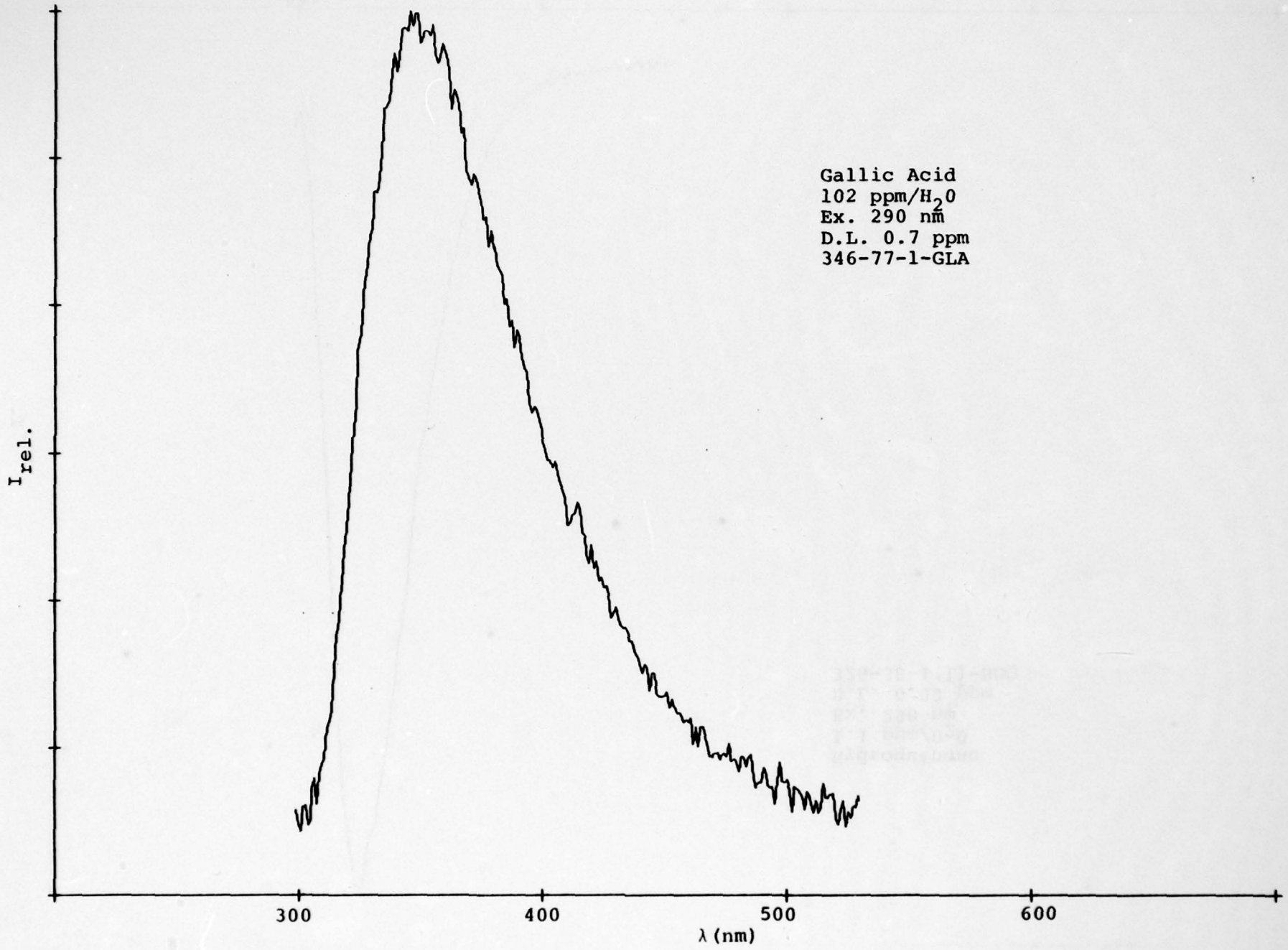

Dodecylbenzene
116 ppm/CH
Ex. 220 nm
D.L. 10 ppm
285-30-3-DDB
$I_{rel.}$
300
400
500
600
λ (nm)

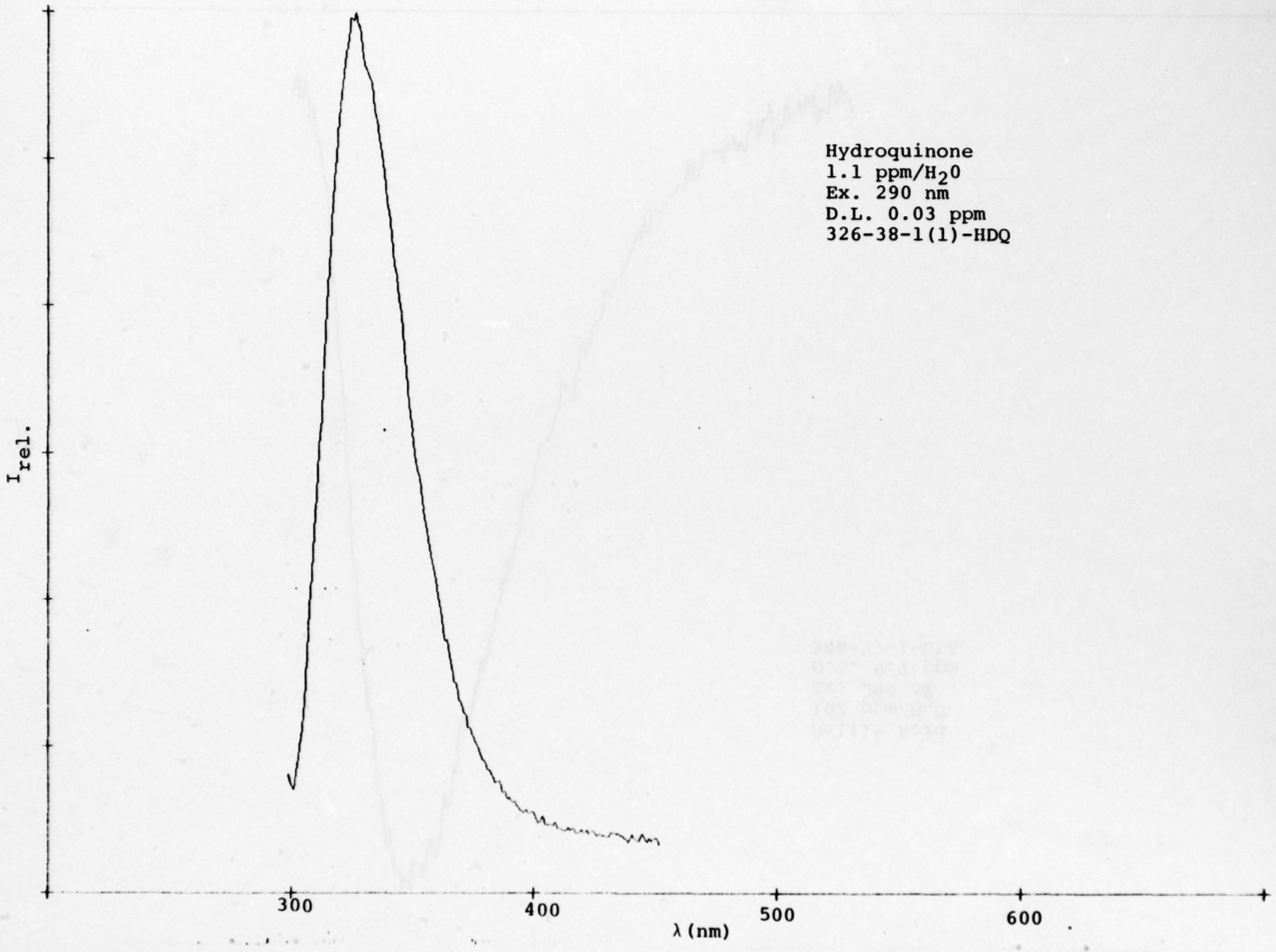

Impurity Emission
Dodecyl benzene
116 ppm/CH
Ex. 250 nm
$I_{rel.}$
Dodecylbenzene
300
400
500
600
λ (nm)

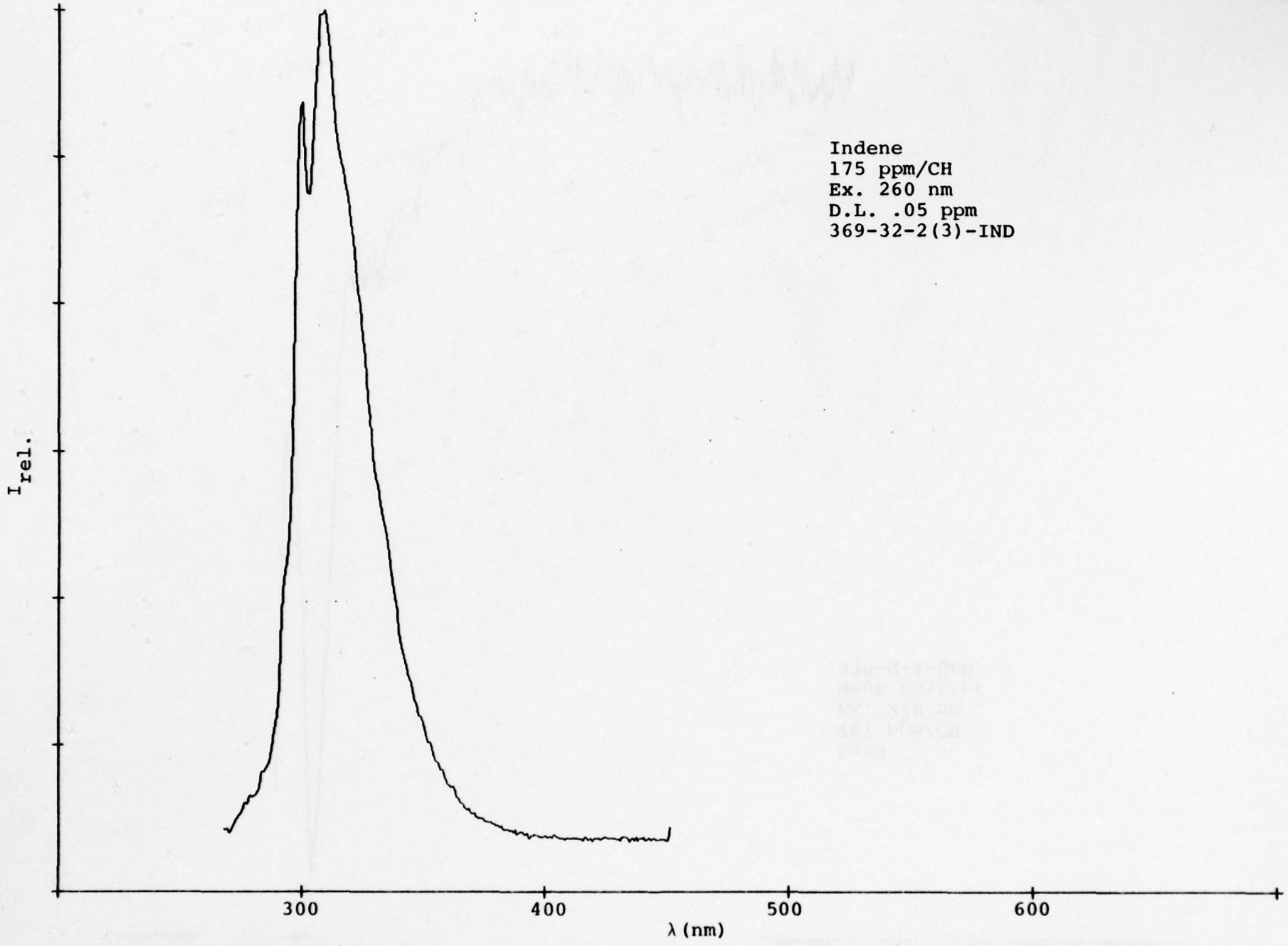

Dowtherm
11 ppm/CH
Ex. 260 nm
D.L. 0.04 ppm
305-30-2(2)-DOW
I rel.
300
400
500
600
λ (nm)

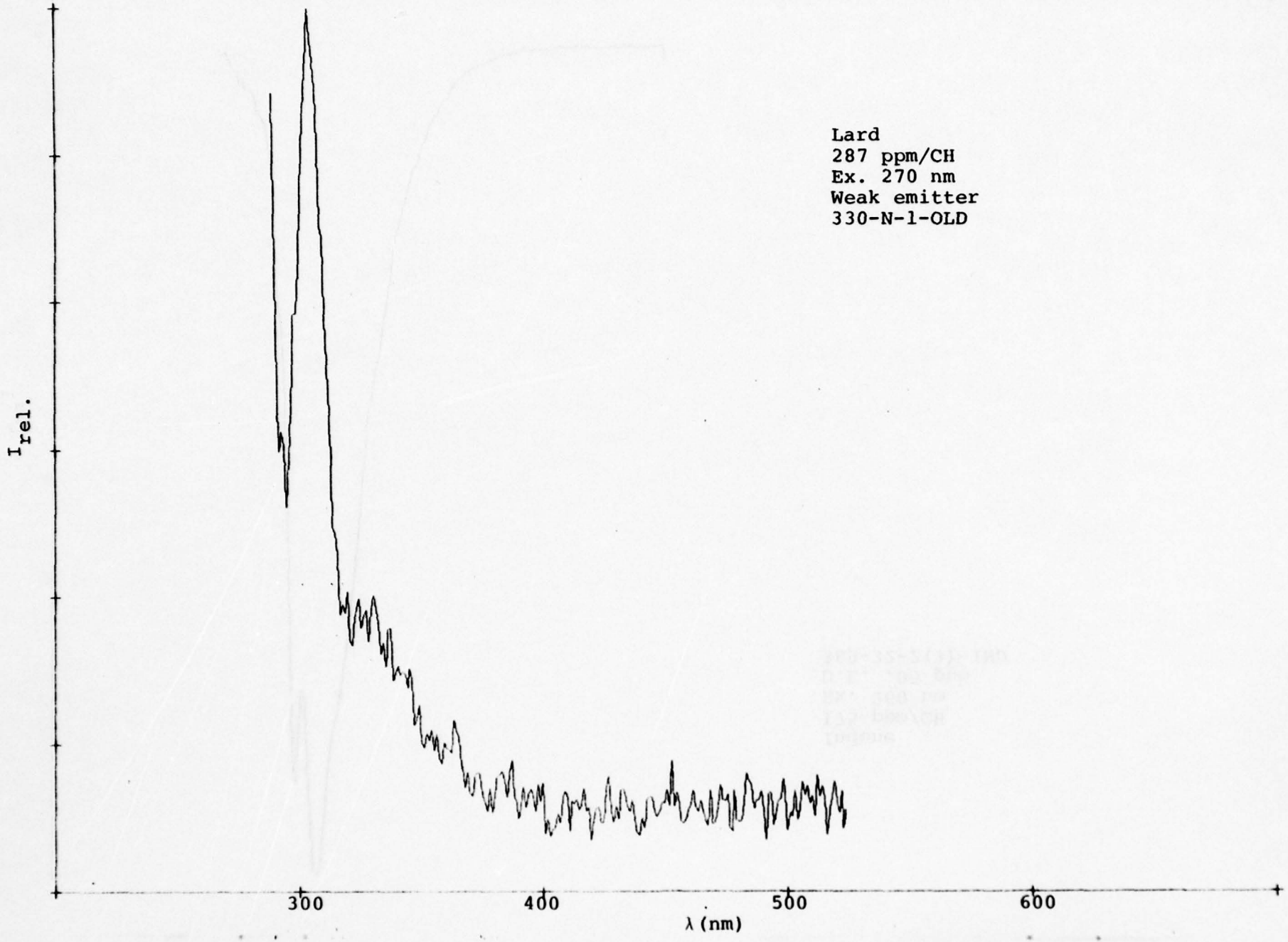

Ethylbenzene
103 ppm/CH
Ex. 250 nm
D.L. 2.0 ppm
283-26-2(2)-ETB
I rel.
300
400
500
600
λ (nm)

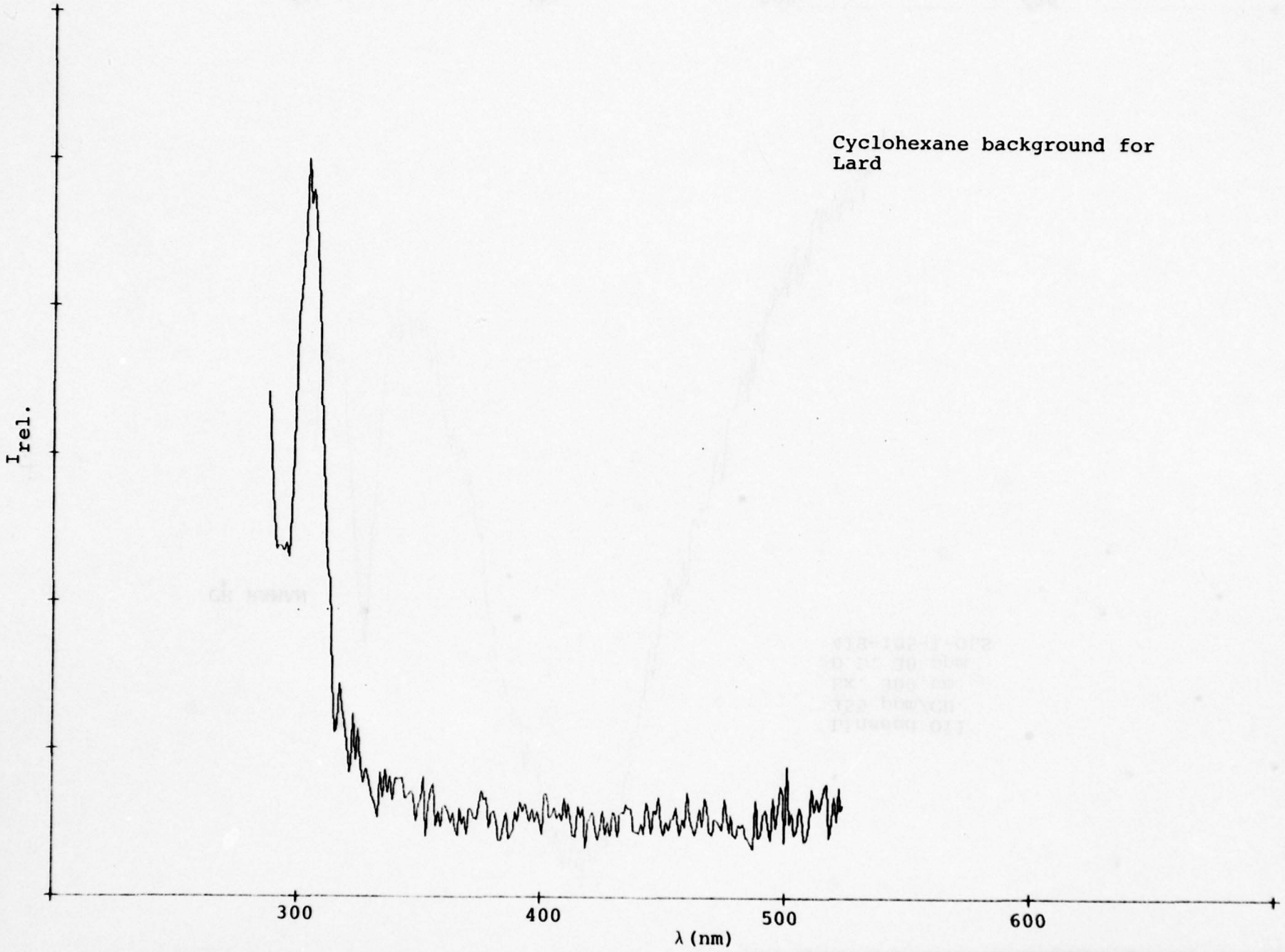

Fluoranthene
1.00 ppm/CH
Ex. 360 nm
D.L. .005 ppm
464-91-2(3)-FLA
$I_{rel.}$
300
400
500
600
λ (nm)

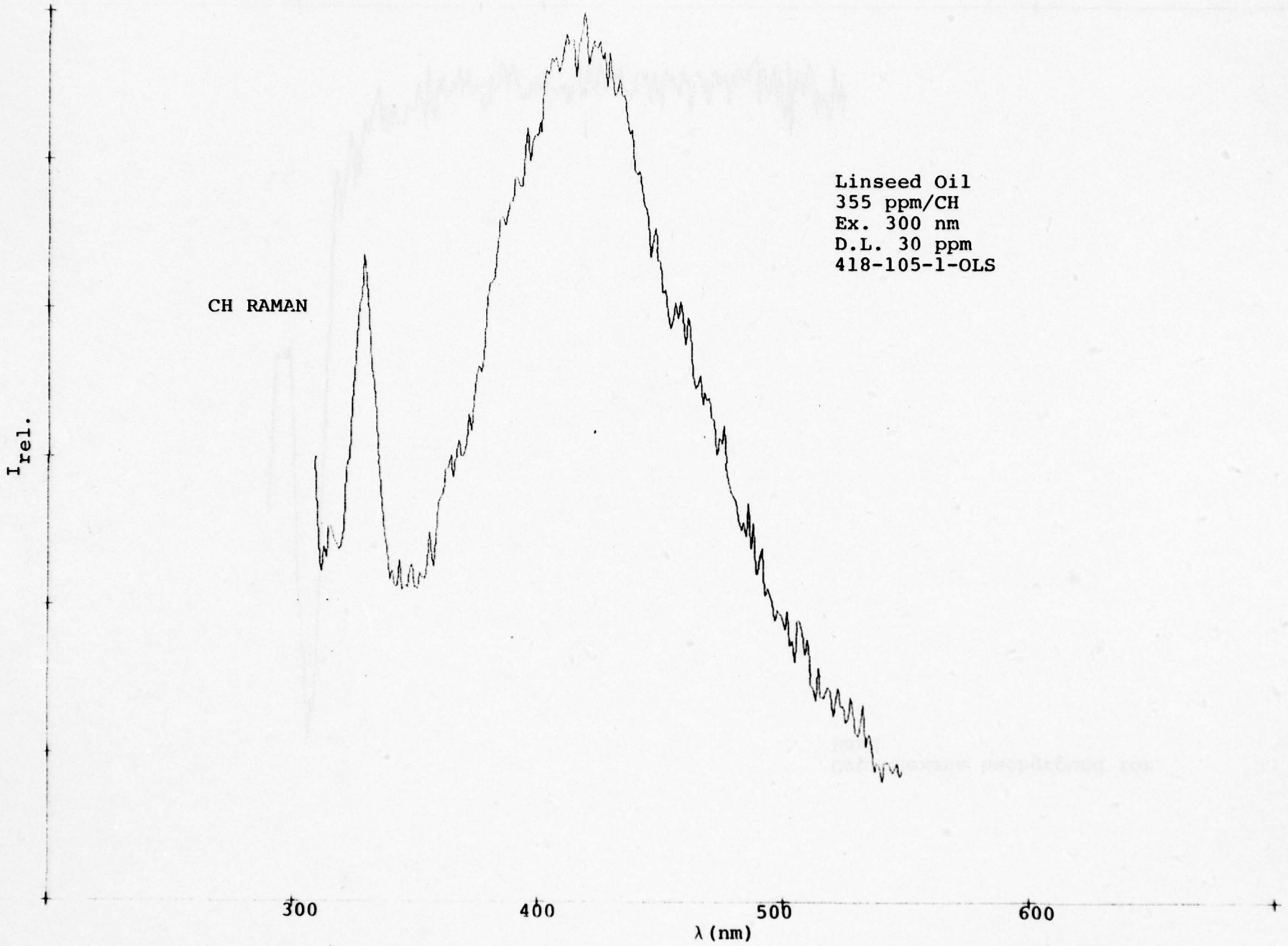

Gallic Acid
102 ppm/H_2O
Ex. 290 nm
D.L. 0.7 ppm
346-77-1-GLA
$I_{rel.}$
300
400
500
600
λ (nm)


Hydroquinone
1.1 ppm/H_2O
Ex. 290 nm
D.L. 0.03 ppm
326-38-1(1)-HDQ
$I_{rel.}$
300
400
500
600
λ (nm)

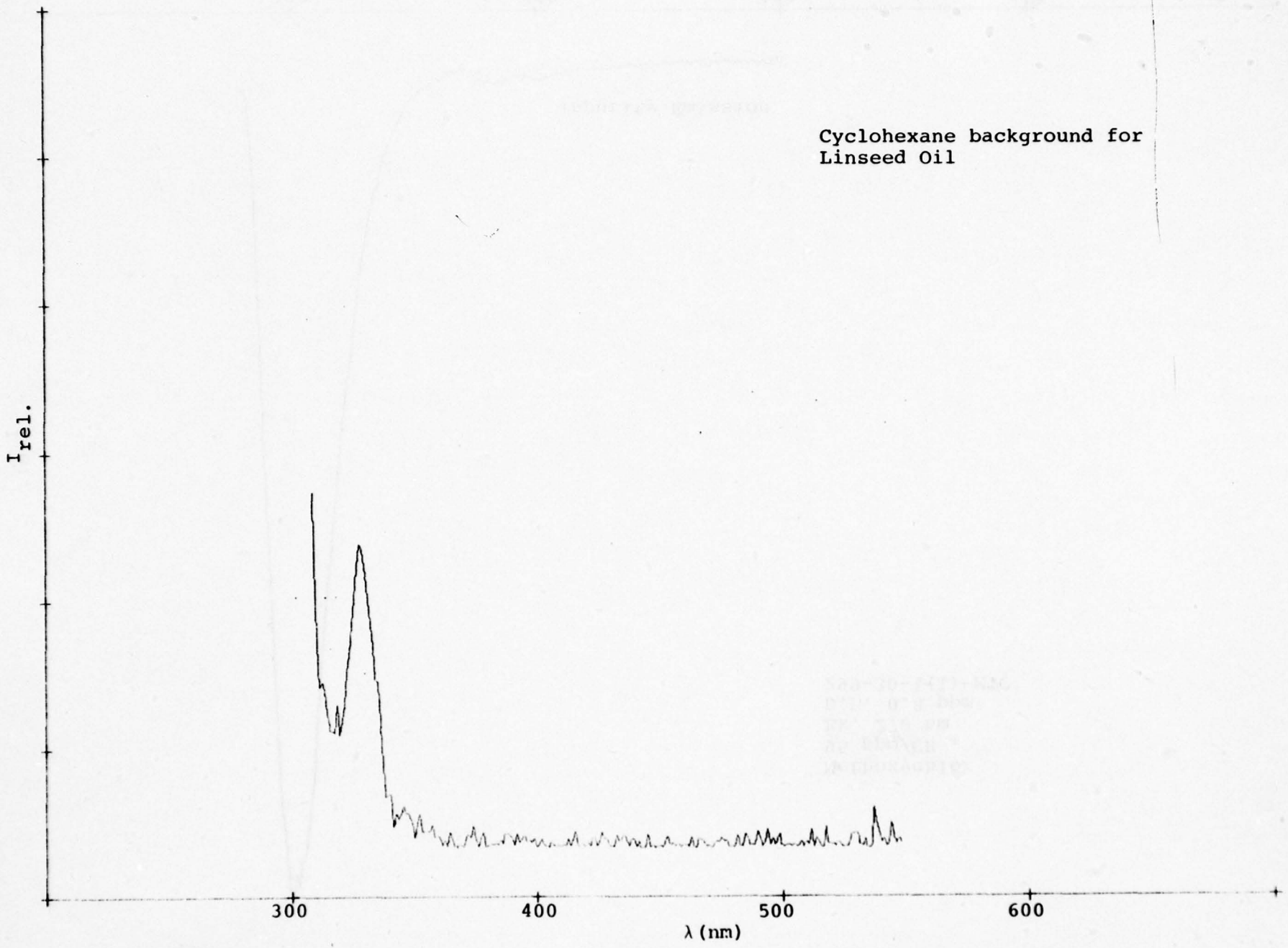

Indene
175 ppm/CH
Ex. 260 nm
D.L. .05 ppm
369-32-2(3)-IND
$I_{rel.}$
300
400
500
600
λ (nm)

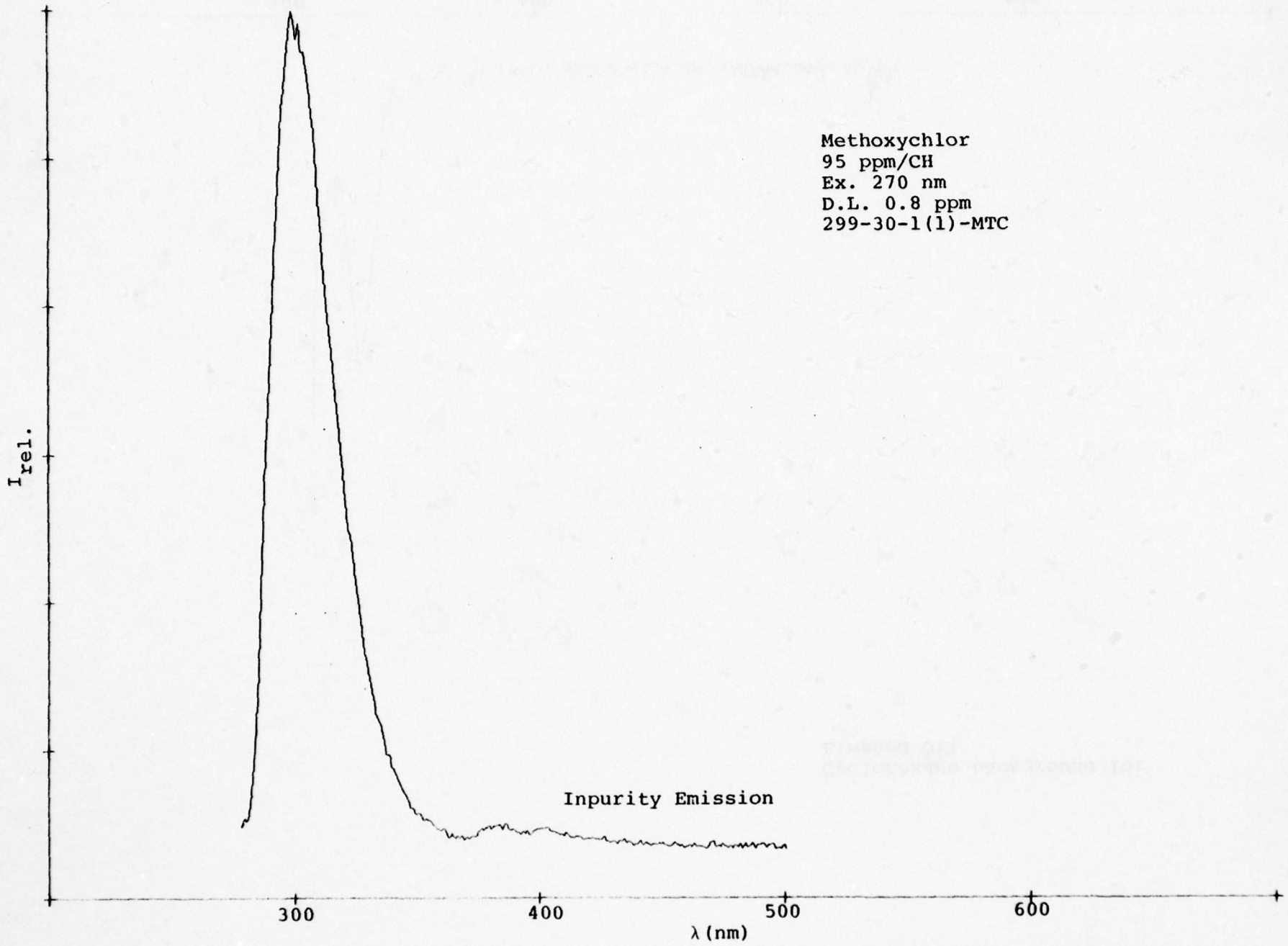

Lard
287 ppm/CH
Ex. 270 nm
Weak emitter
330-N-1-OLD
I rel.
300
400
500
600
λ (nm)

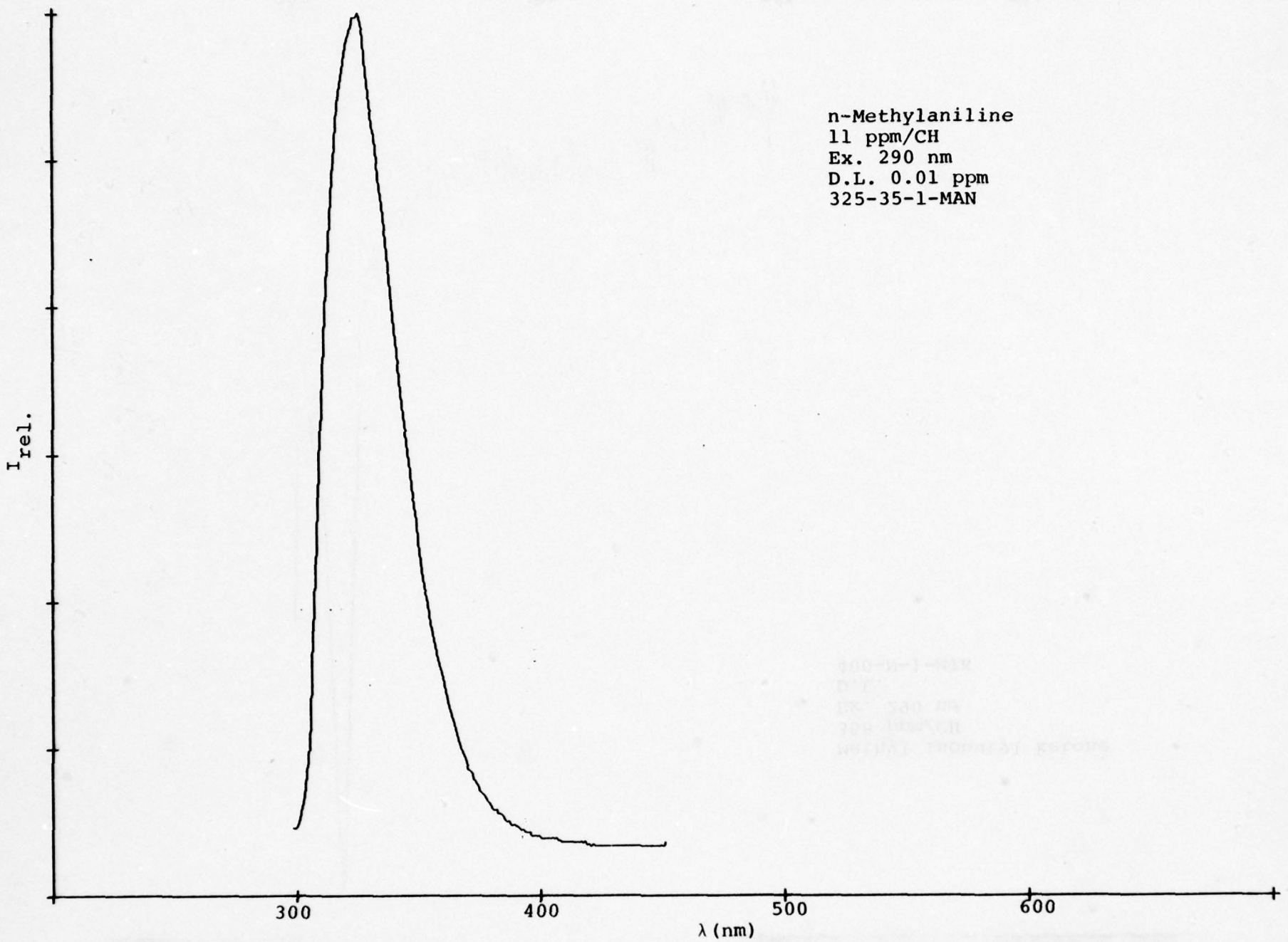

Cyclohexane background for
Lard
I rel.
300
400
500
600
λ (nm)

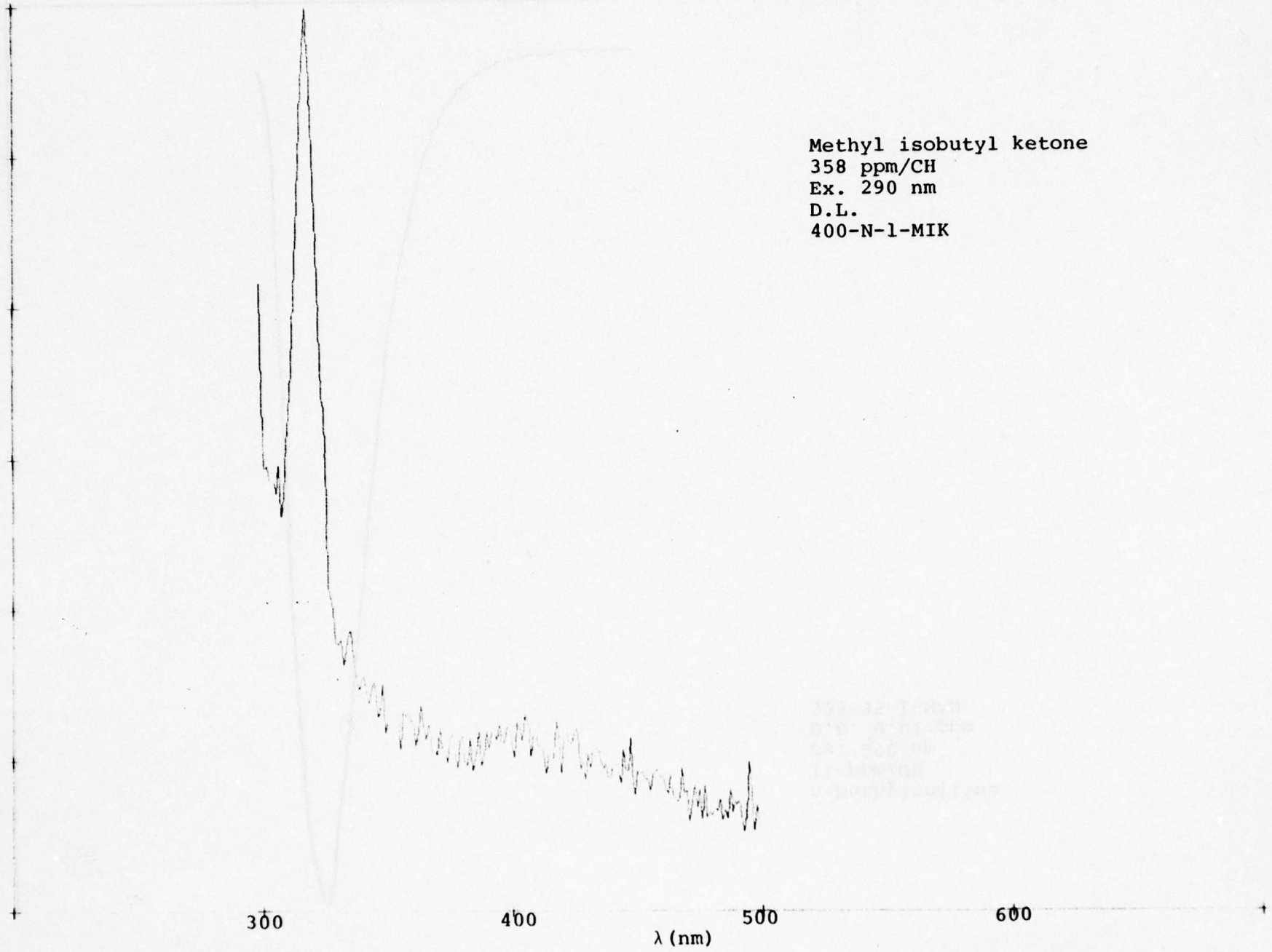

Linseed Oil
355 ppm/CH
Ex. 300 nm
D.L. 30 ppm
418-105-1-OLS
CH RAMAN
$I_{rel.}$
300
400
500
600
λ (nm)

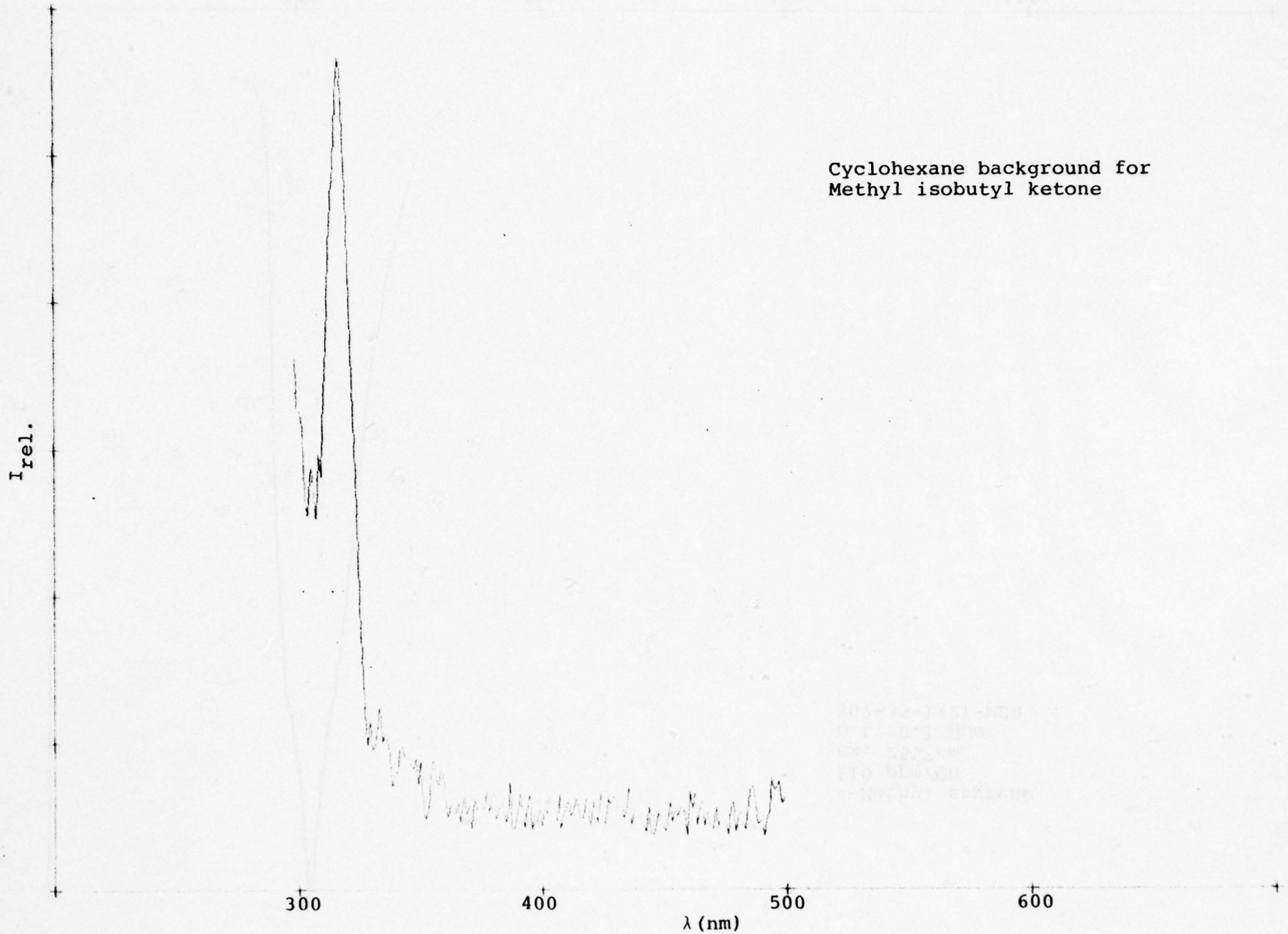
Cyclohexane background for
Linseed Oil



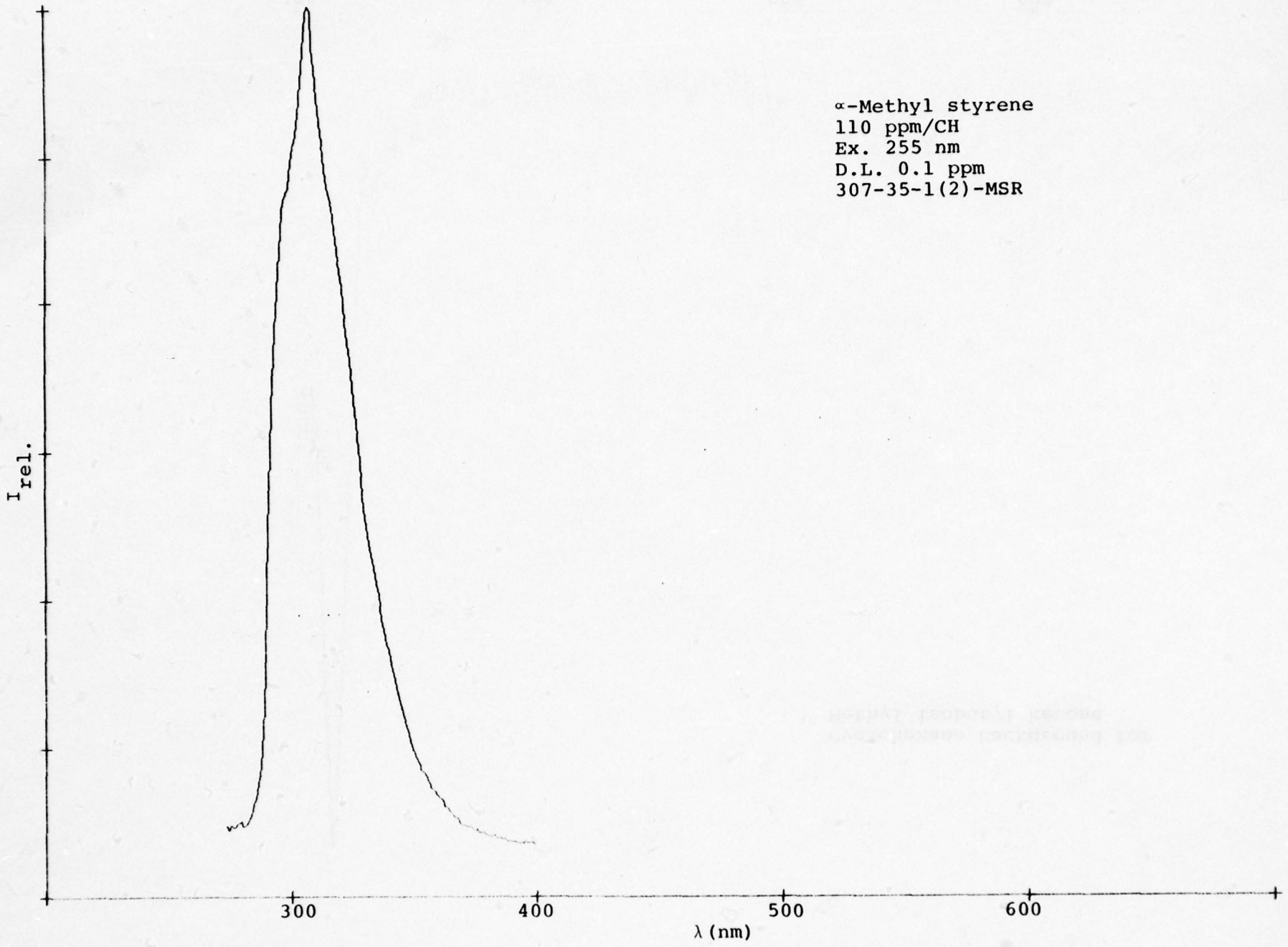

Methoxychlor
95 ppm/CH
Ex. 270 nm
D.L. 0.8 ppm
299-30-1(1)-MTC
$I_{rel.}$
Inpurity Emission
300
400
500
600
λ (nm)

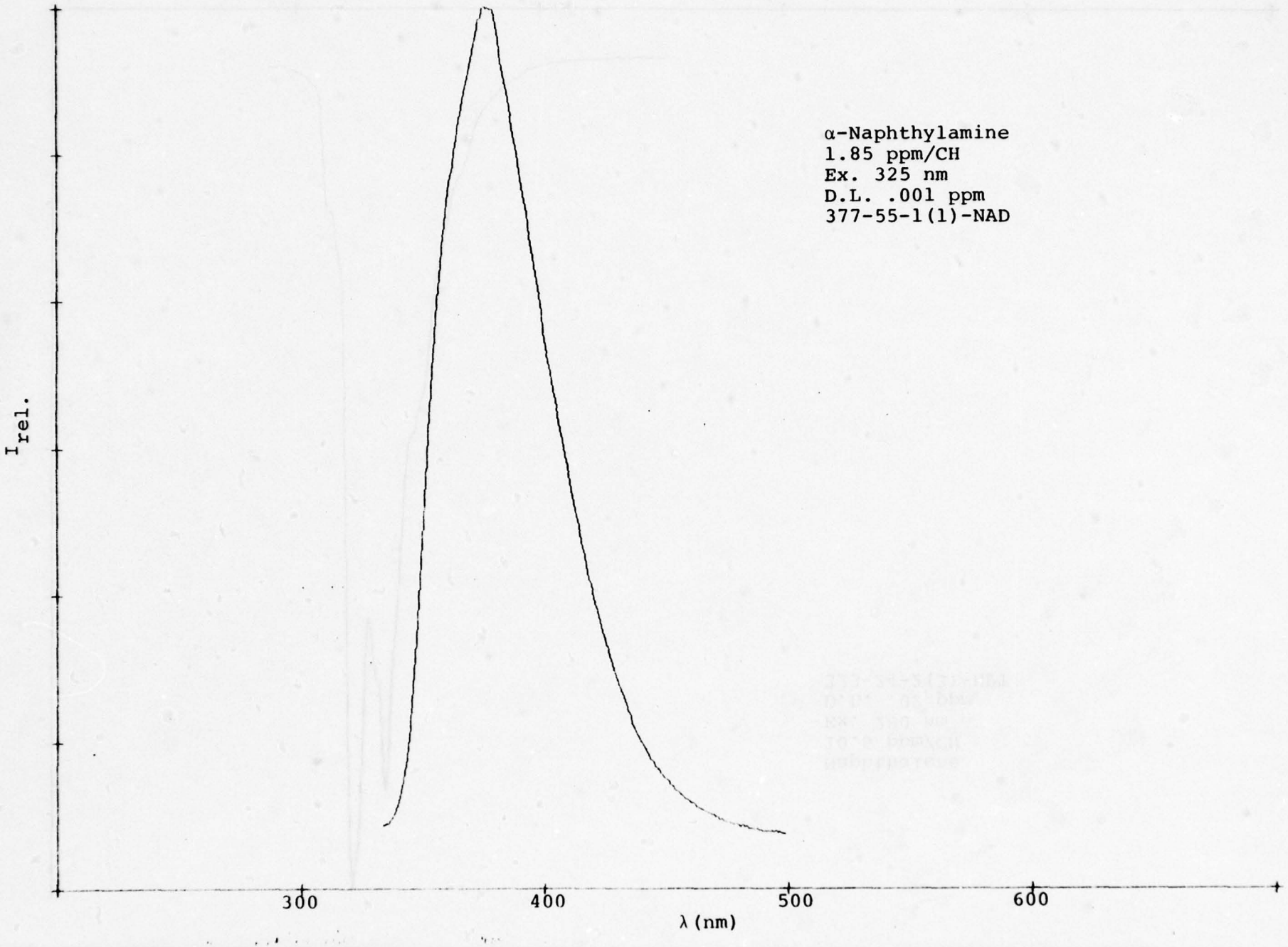

n-Methylaniline
11 ppm/CH
Ex. 290 nm
D.L. 0.01 ppm
325-35-1-MAN
I rel.
300
400
500
600
λ (nm)

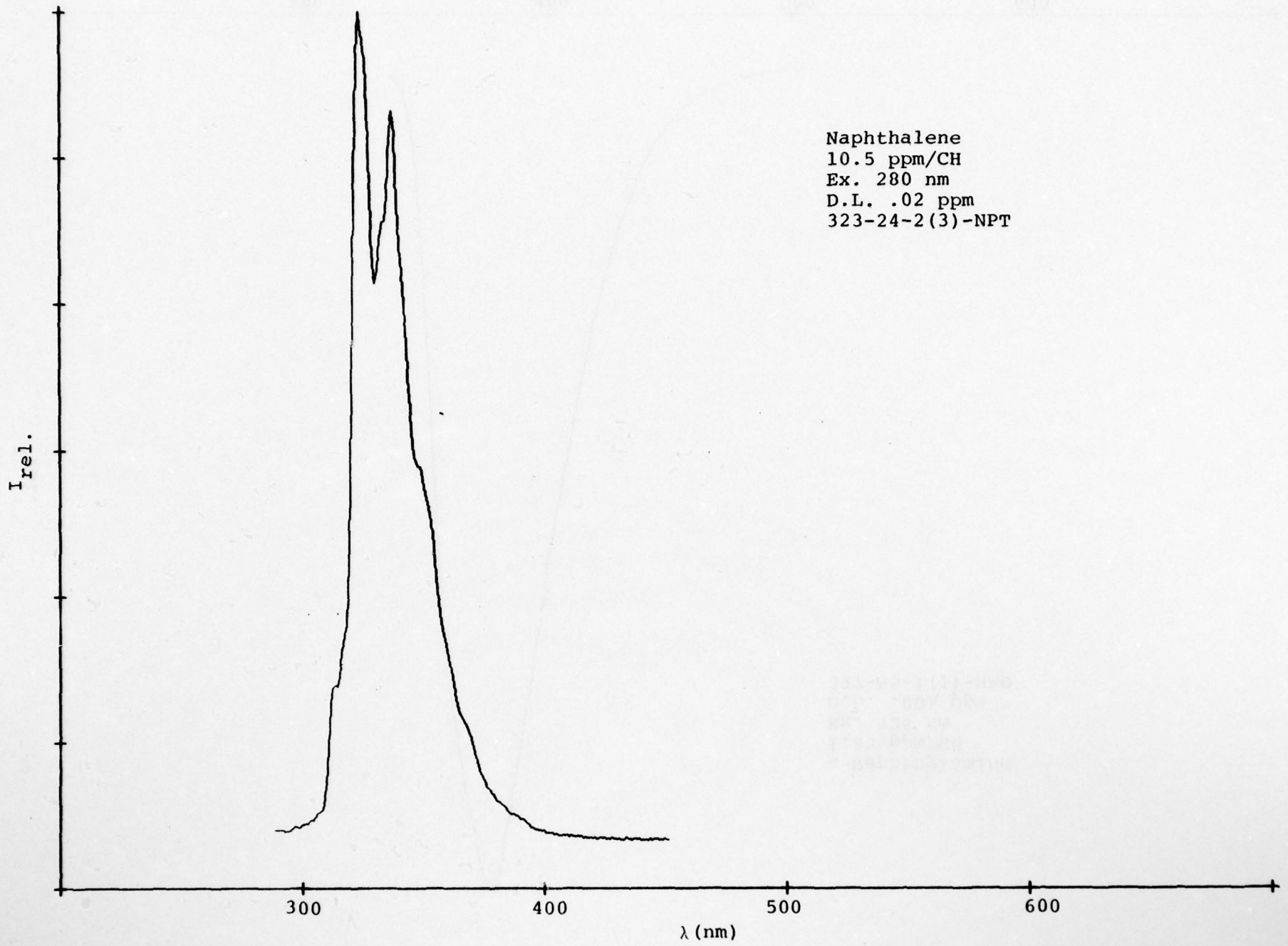

Methyl isobutyl ketone
358 ppm/CH
Ex. 290 nm
D.L.
400-N-1-MIK
300
400
500
600
λ (nm)

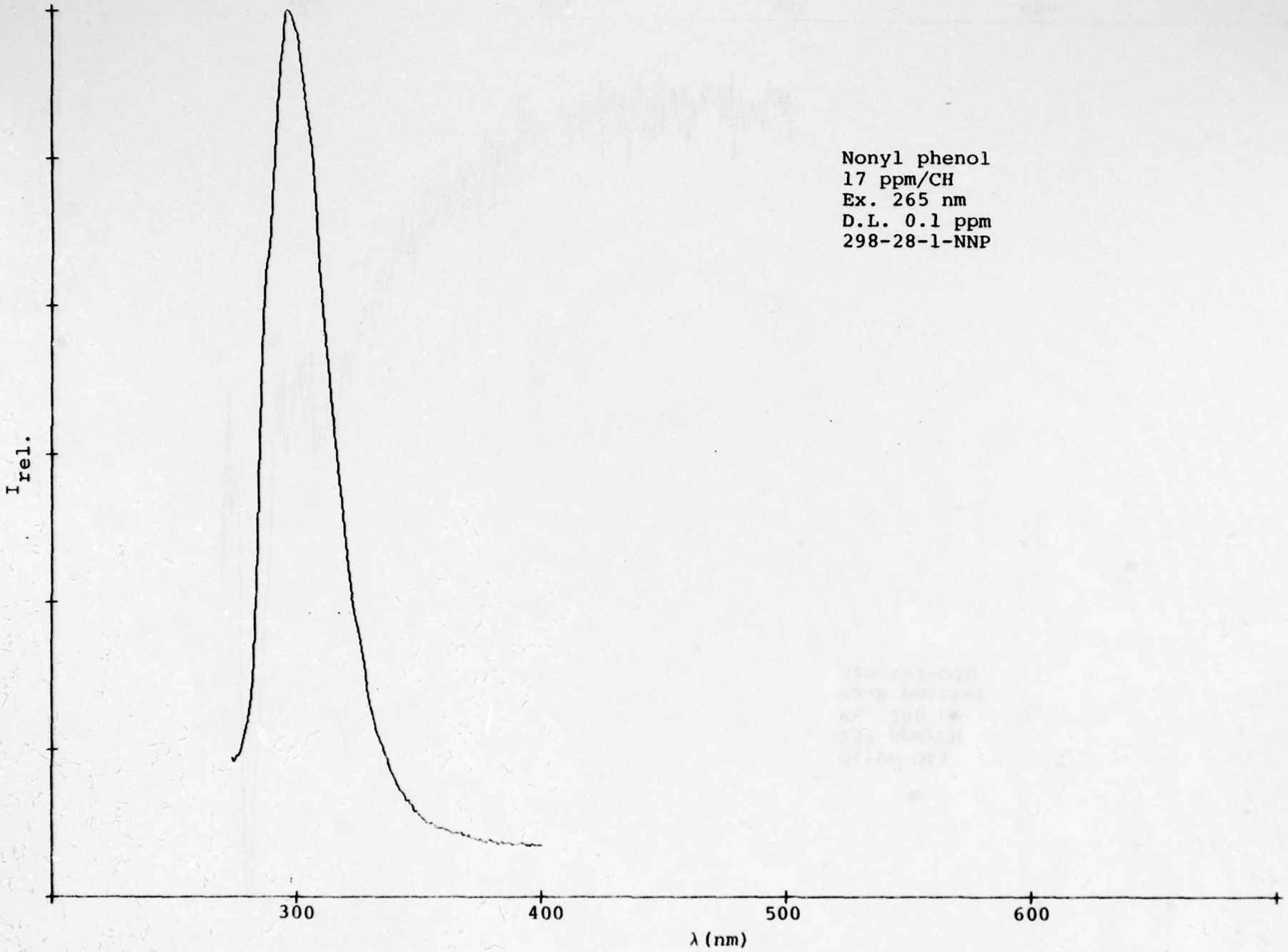


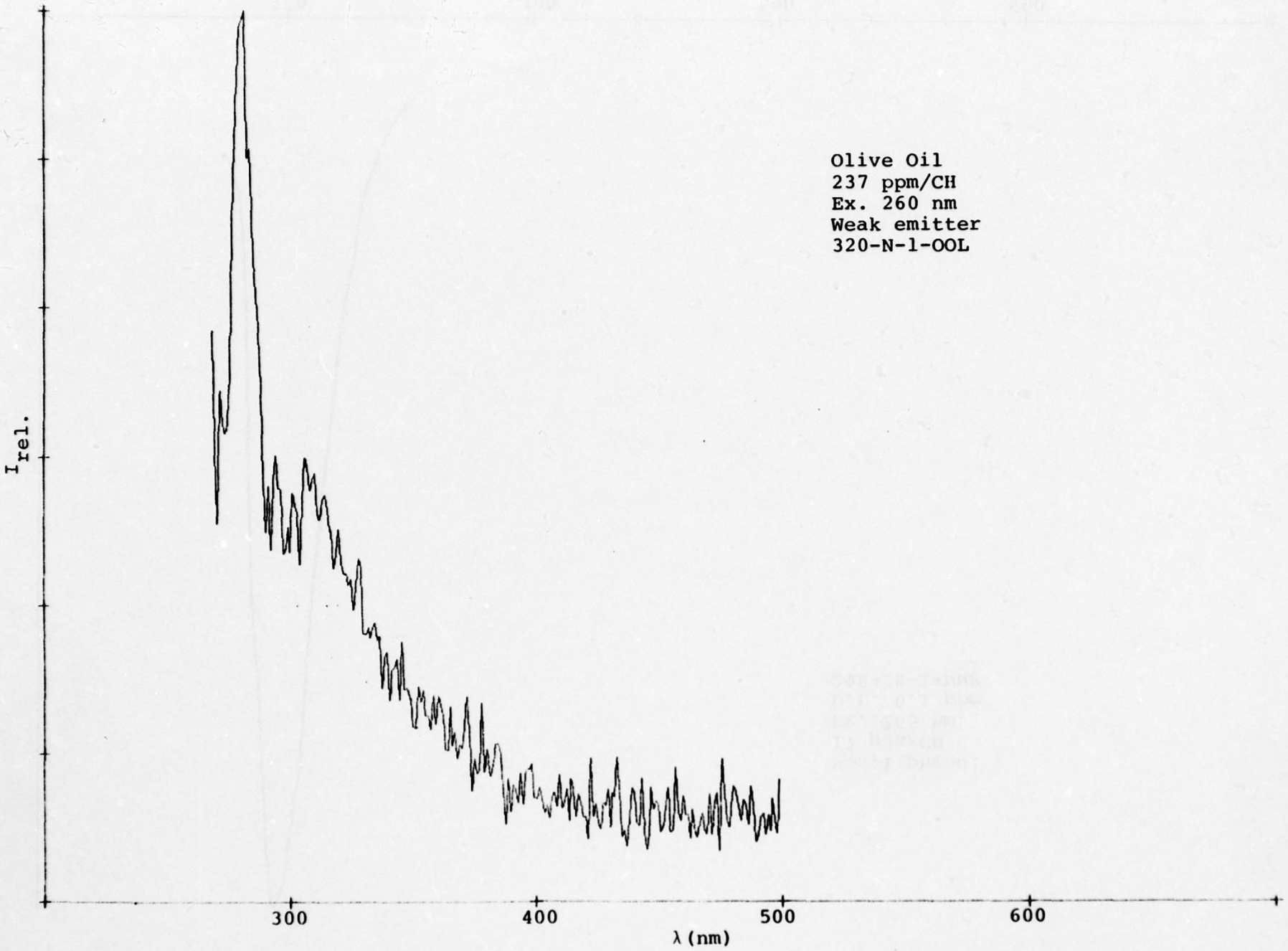
Cyclohexane background for
Methyl isobutyl ketone

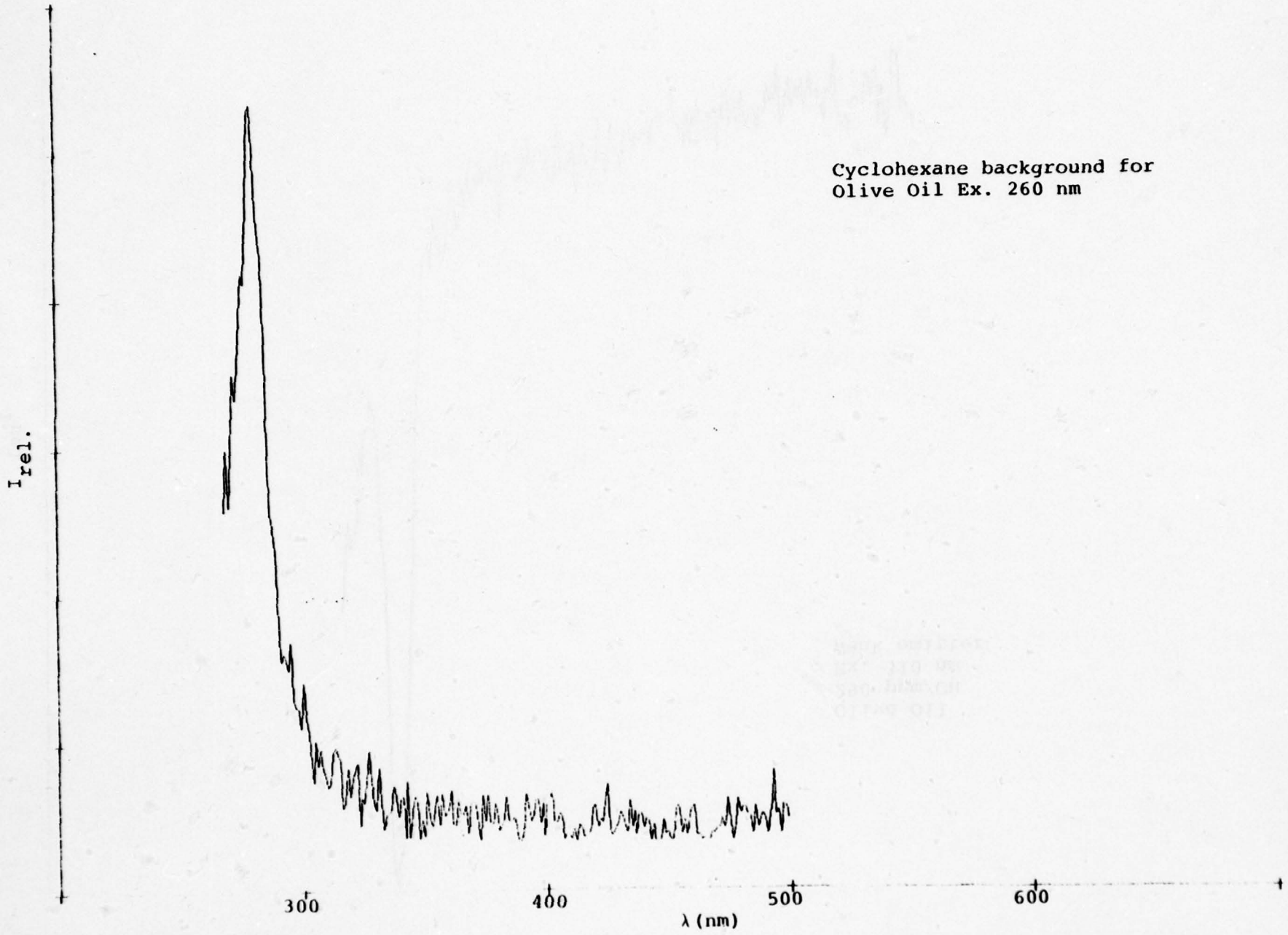

α-Methyl styrene
110 ppm/CH
Ex. 255 nm
D.L. 0.1 ppm
307-35-1(2)-MSR
I rel.
300
400
500
600
λ (nm)

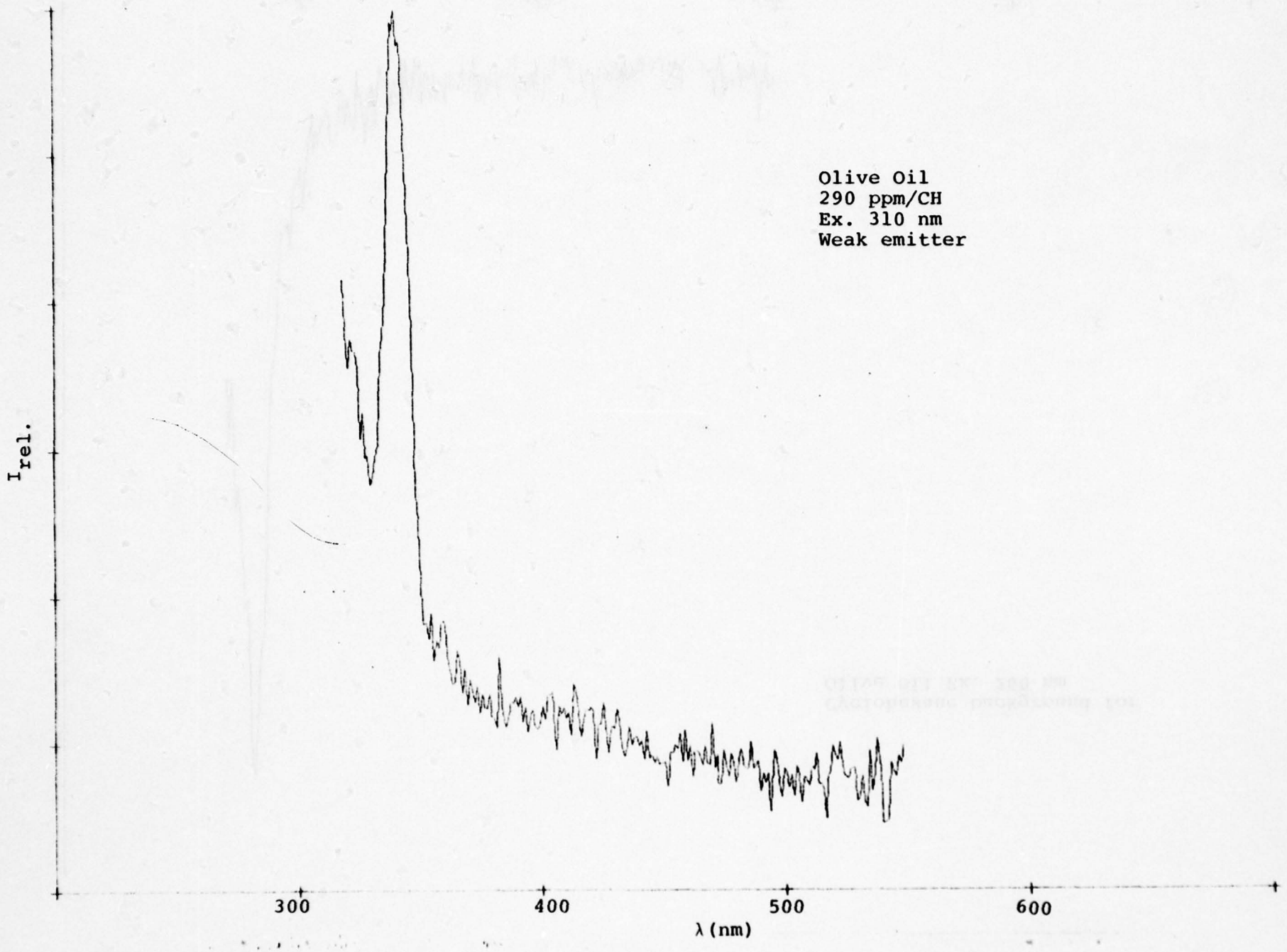

α-Naphthylamine
1.85 ppm/CH
Ex. 325 nm
D.L. .001 ppm
377-55-1(1)-NAD
$I_{rel.}$
300
400
500
600
λ (nm)

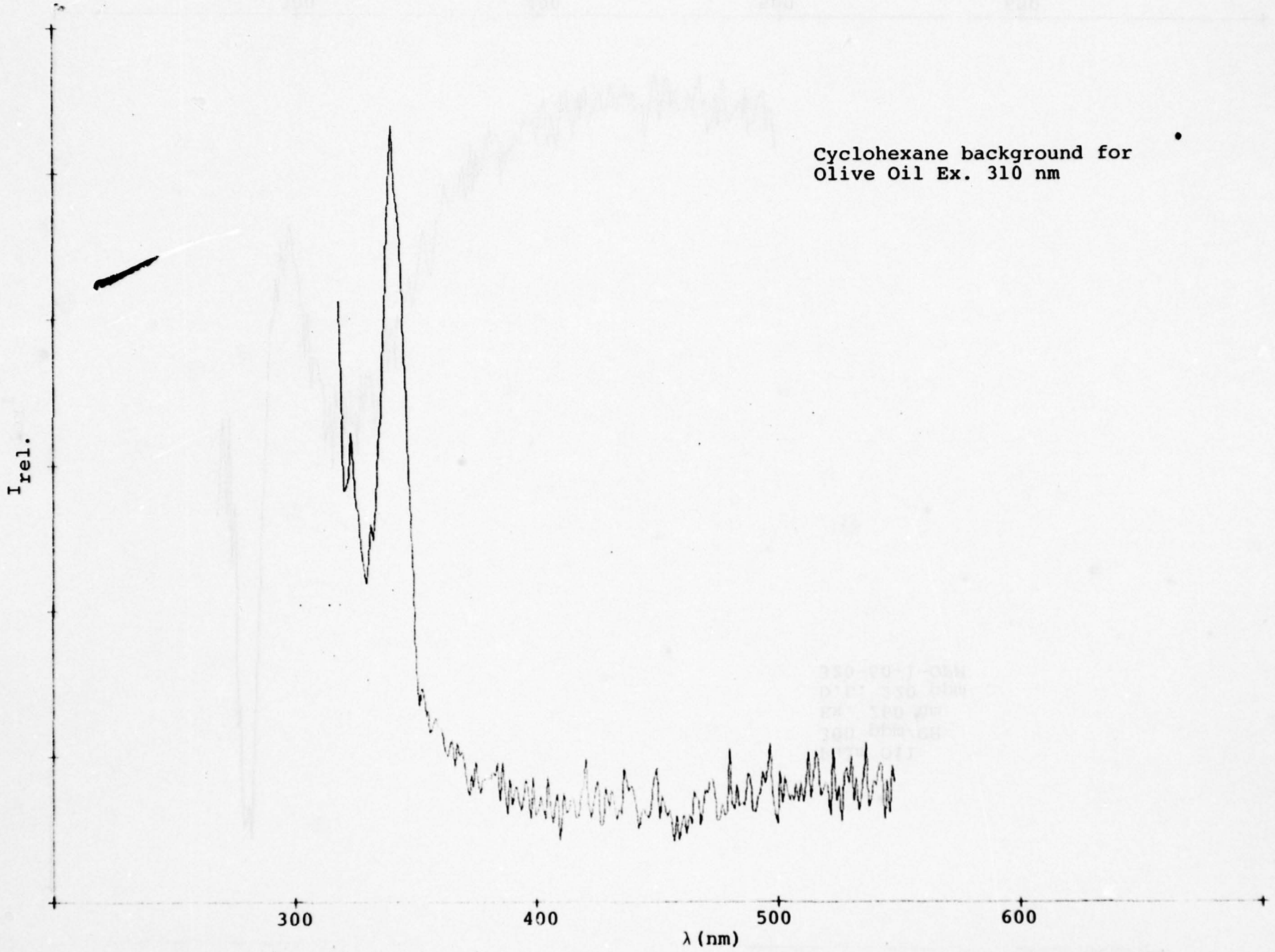

Naphthalene
10.5 ppm/CH
Ex. 280 nm
D.L. .02 ppm
323-24-2(3)-NPT
$I_{rel.}$
300
400
500
600
λ (nm)

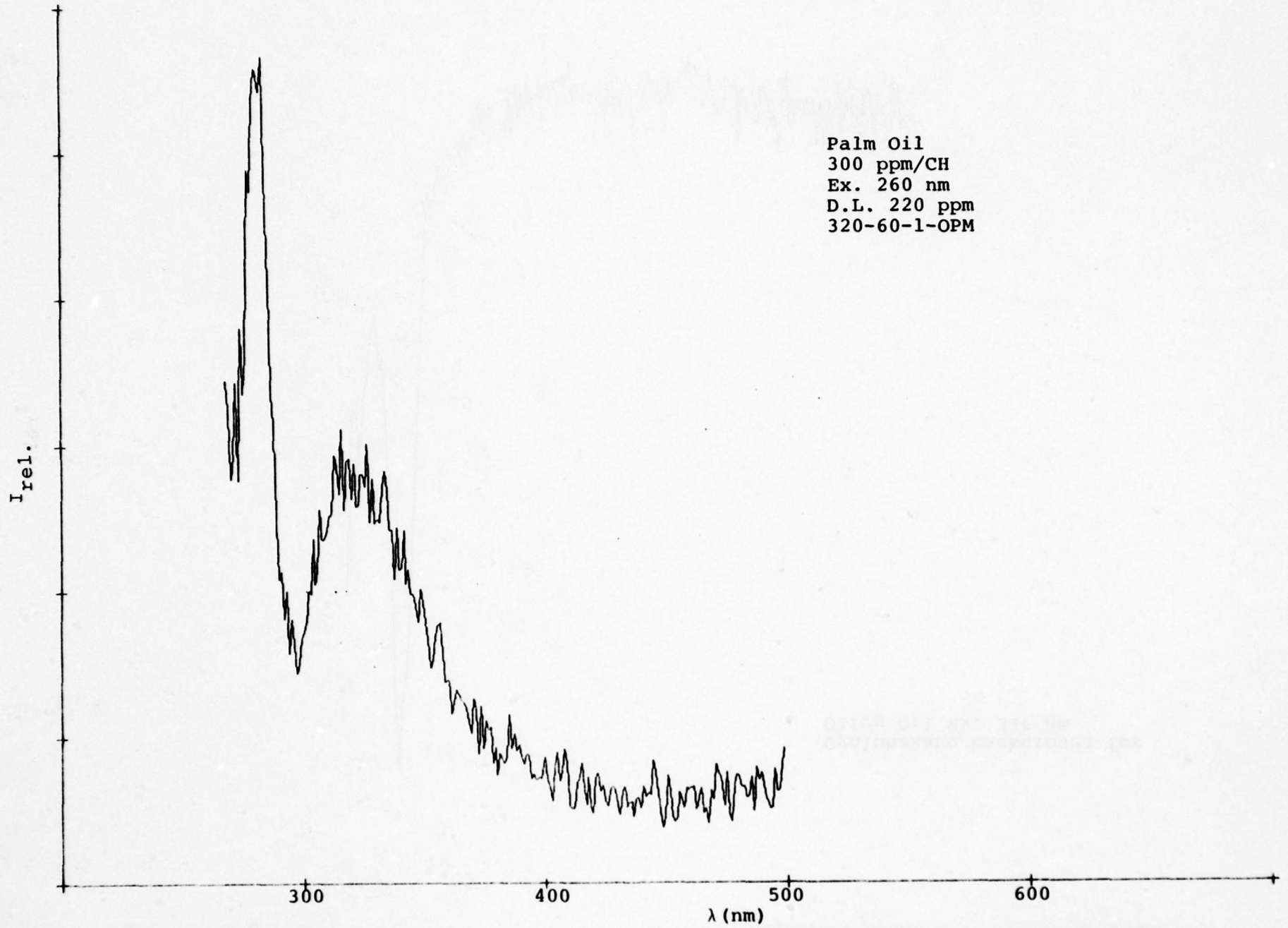

Nonyl phenol
17 ppm/CH
Ex. 265 nm
D.L. 0.1 ppm
298-28-1-NNP
I rel.
300
400
500
600
λ (nm)

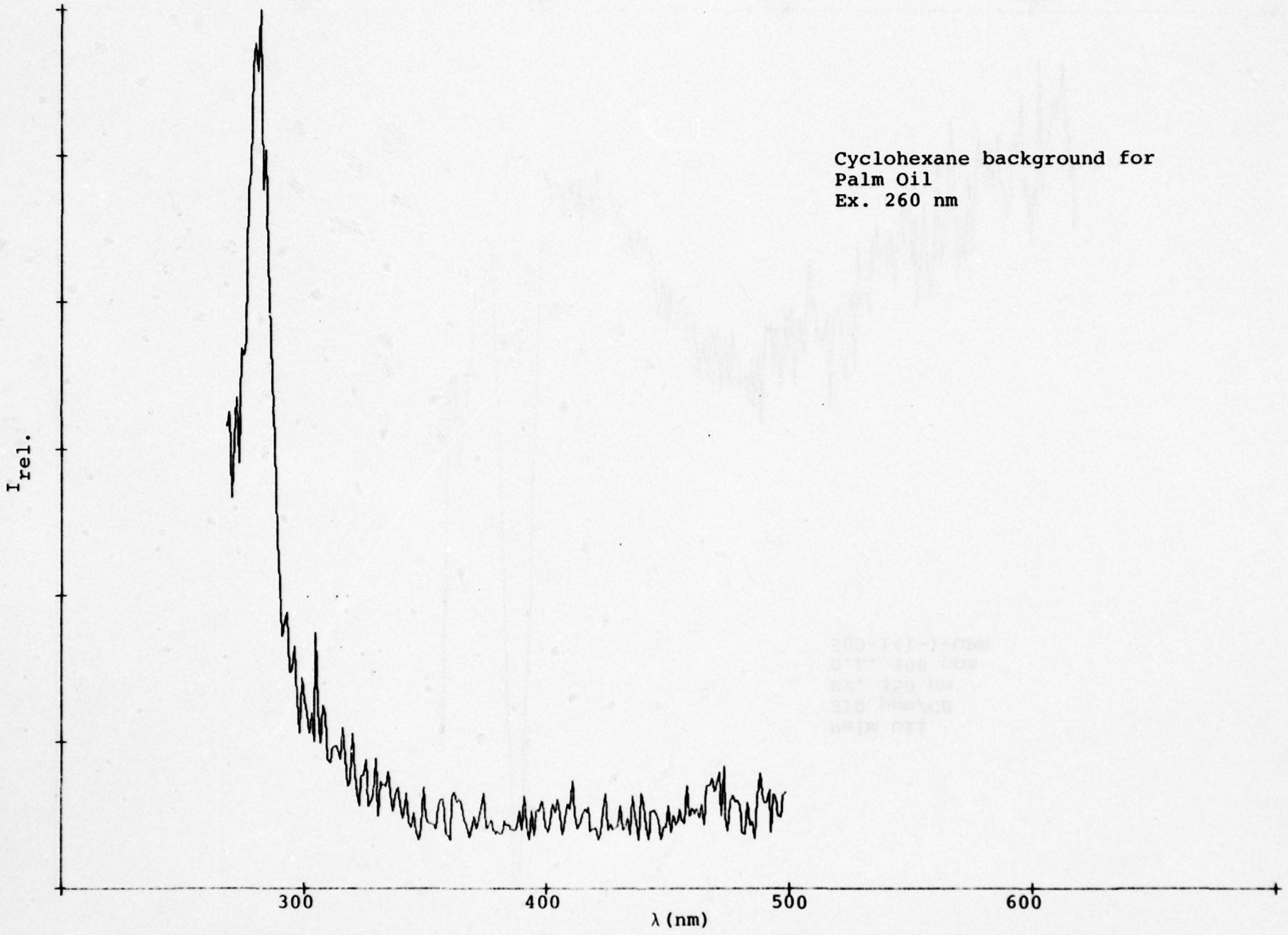

Olive Oil
237 ppm/CH
Ex. 260 nm
Weak emitter
320-N-1-OOL
$I_{rel.}$
300
400
500
600
λ (nm)

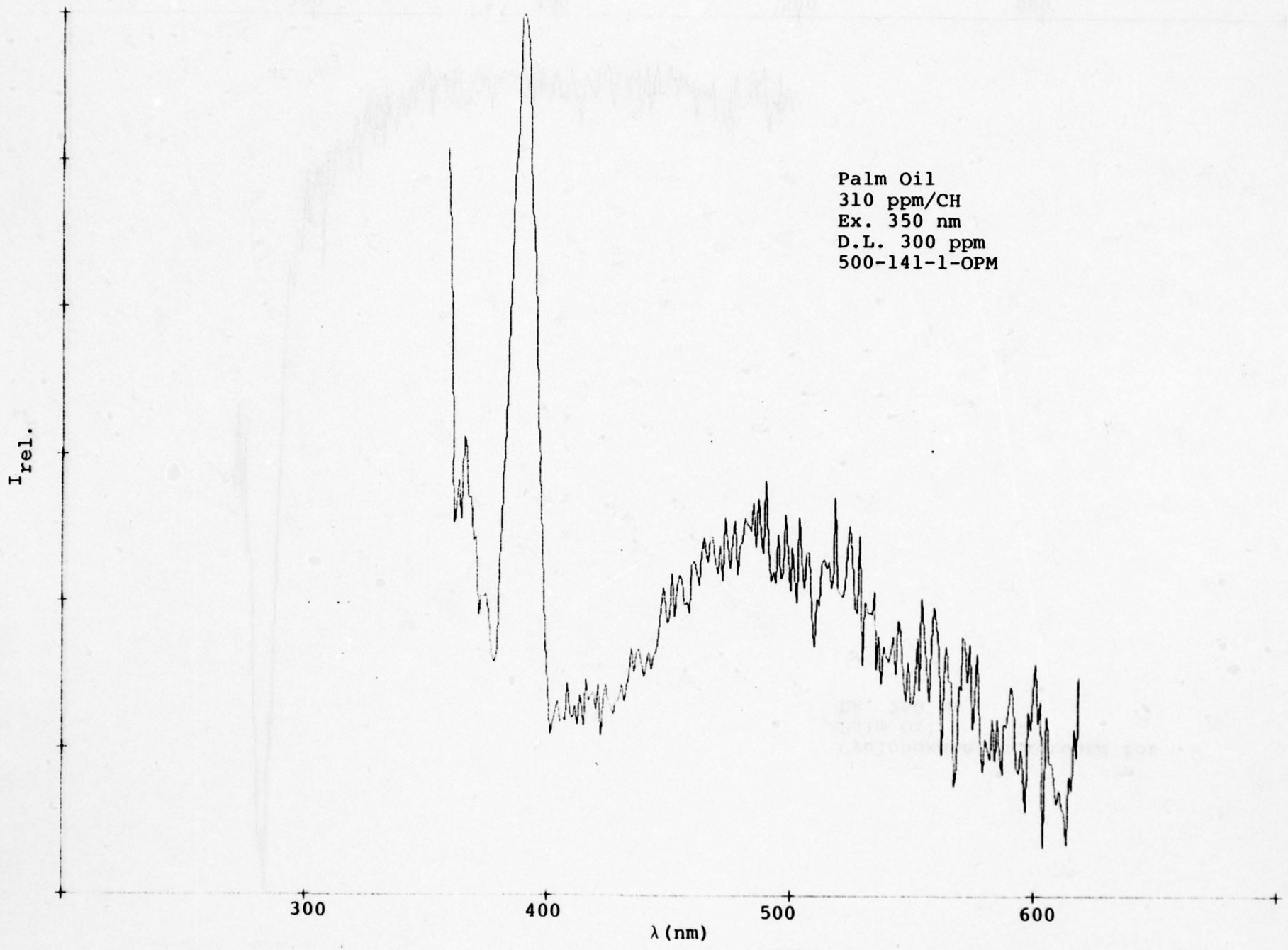

Cyclohexane background for
Olive Oil Ex. 260 nm
$I_{rel.}$
300
400
500
600
λ (nm)

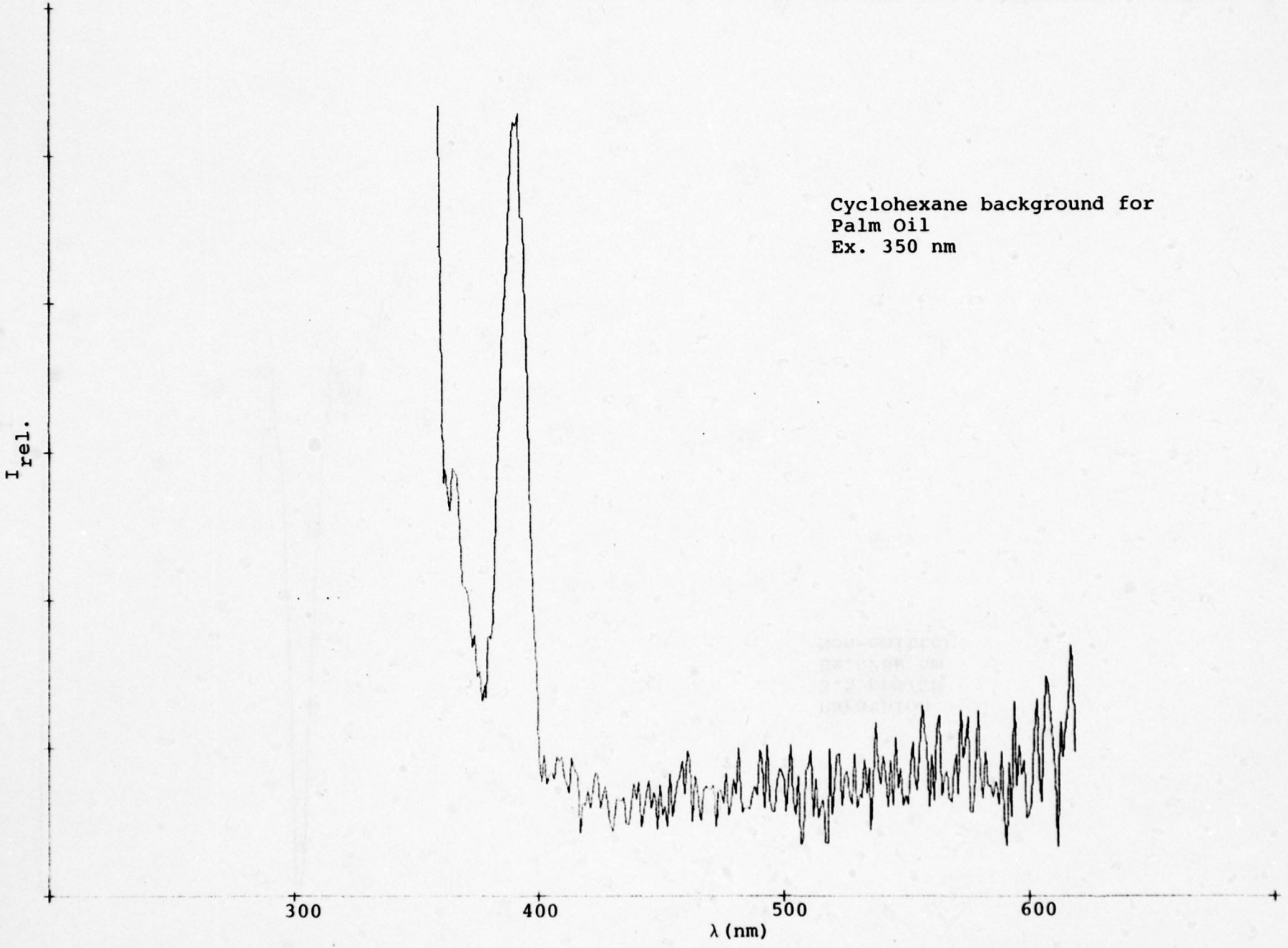

Olive Oil
290 ppm/CH
Ex. 310 nm
Weak emitter
$I_{rel.}$
300
400
500
600
λ (nm)

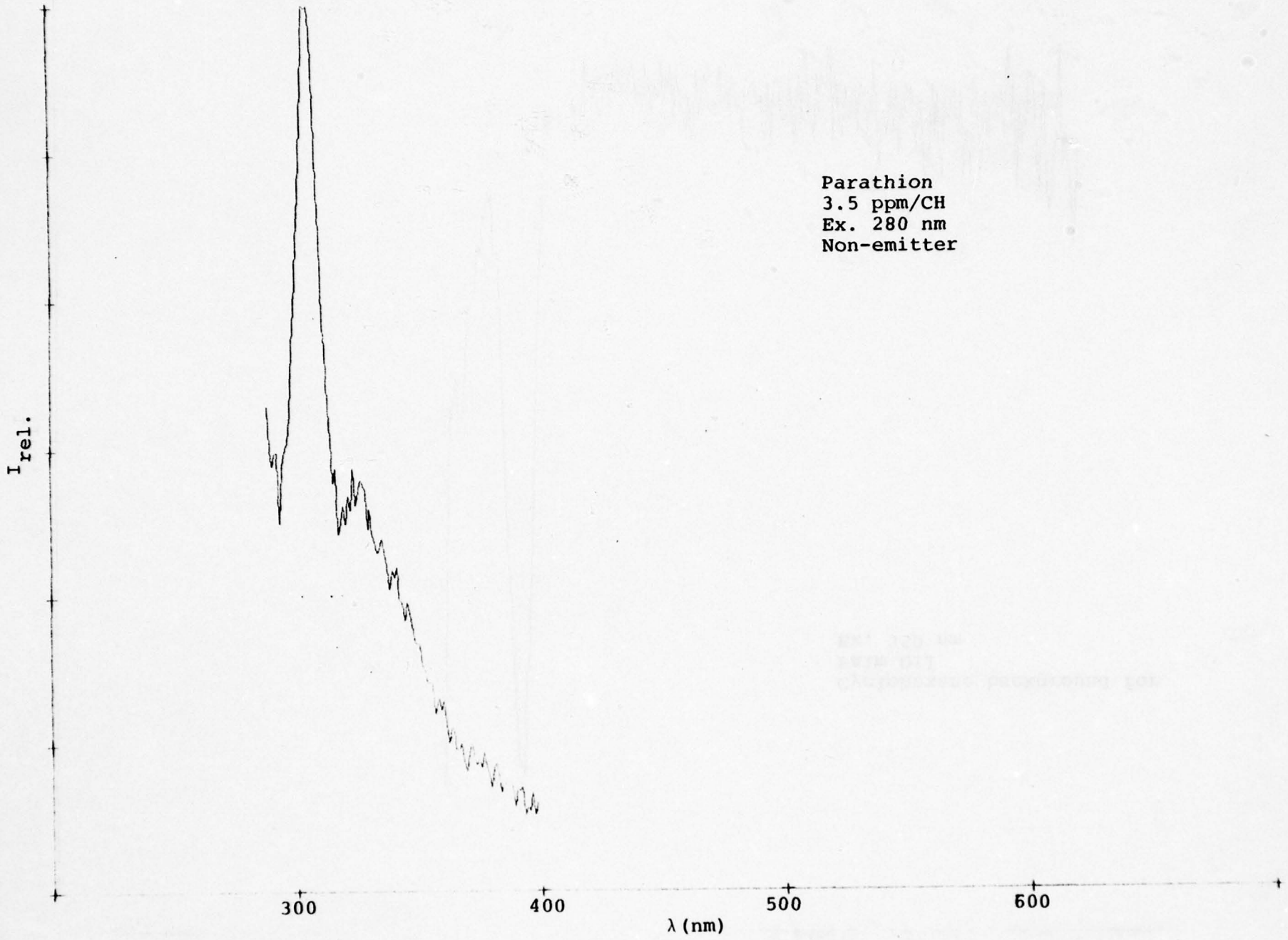

Cyclohexane background for
Olive Oil Ex. 310 nm
$I_{rel.}$
300
400
500
600
λ (nm)

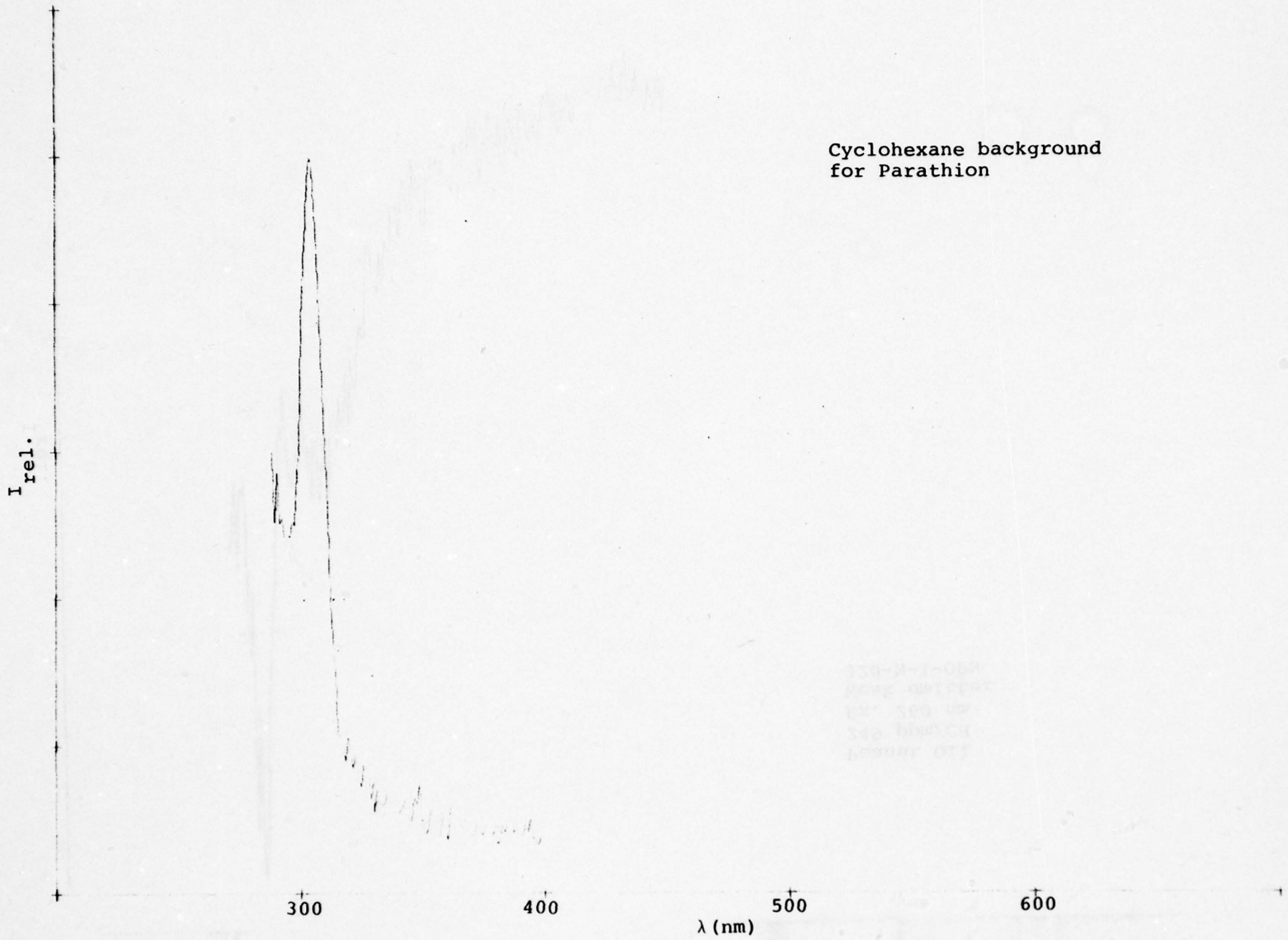

Palm Oil
300 ppm/CH
Ex. 260 nm
D.L. 220 ppm
320-60-1-OPM
$I_{rel.}$
300
400
500
600
λ (nm)


Cyclohexane background for
Palm Oil
Ex. 260 nm
$I_{rel.}$
300
400
500
600
λ (nm)

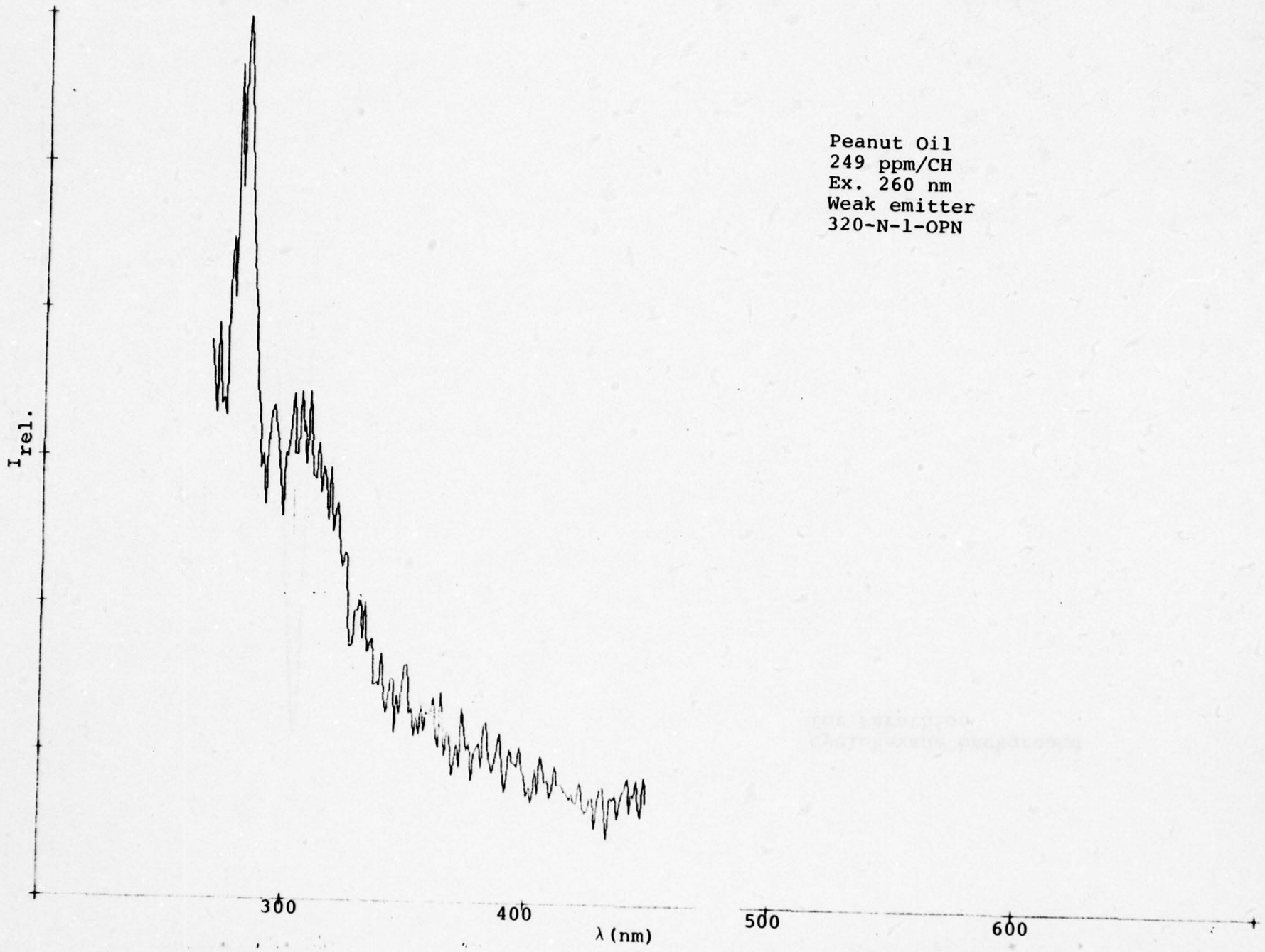

Palm Oil
310 ppm/CH
Ex. 350 nm
D.L. 300 ppm
500-141-1-OPM
$I_{rel.}$
300
400
500
600
λ (nm)

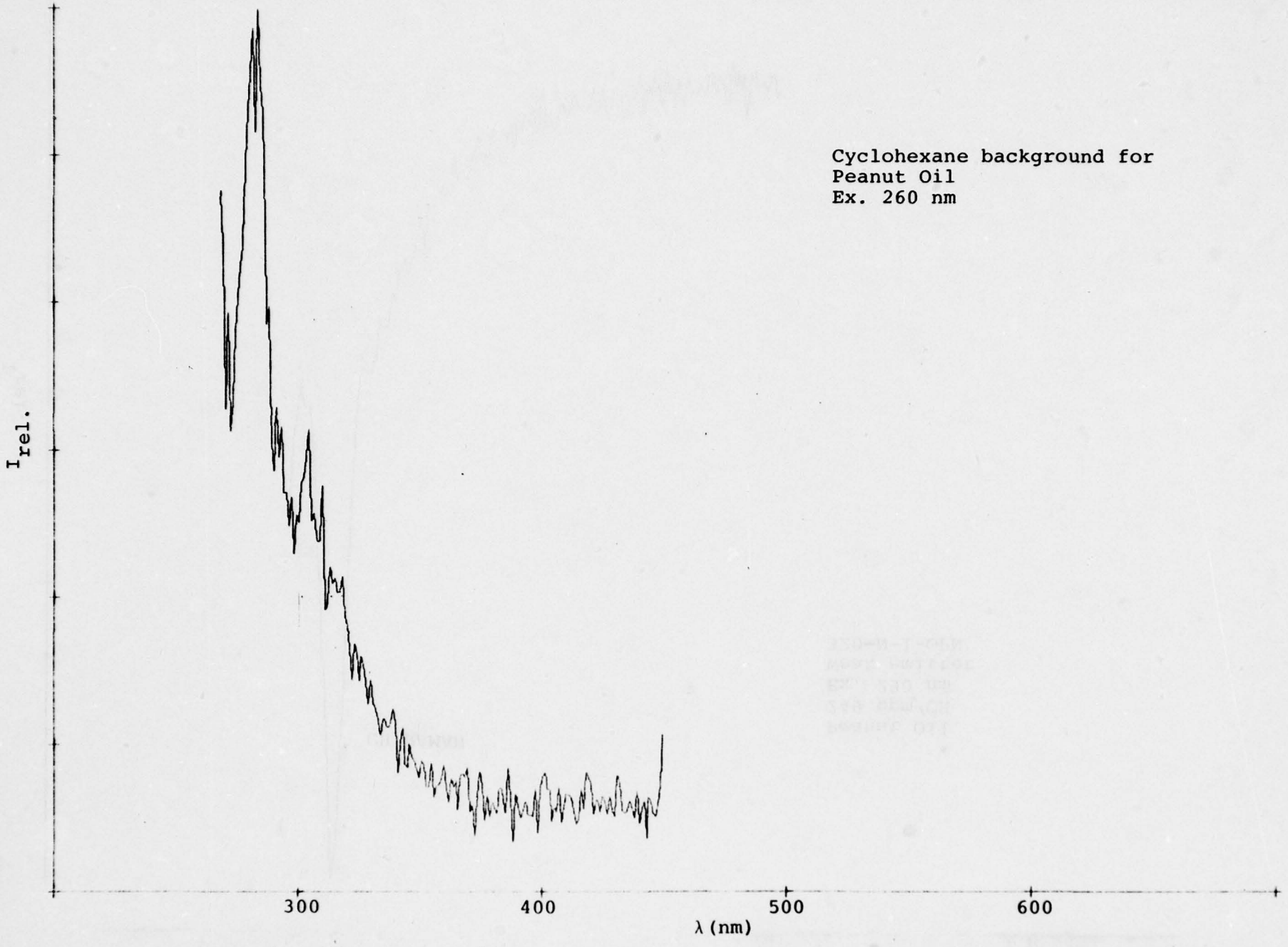

Cyclohexane background for
Palm Oil
Ex. 350 nm
$I_{rel.}$
300
400
500
600
λ (nm)


Parathion
3.5 ppm/CH
Ex. 280 nm
Non-emitter
$I_{rel.}$
300
400
500
600
λ (nm)

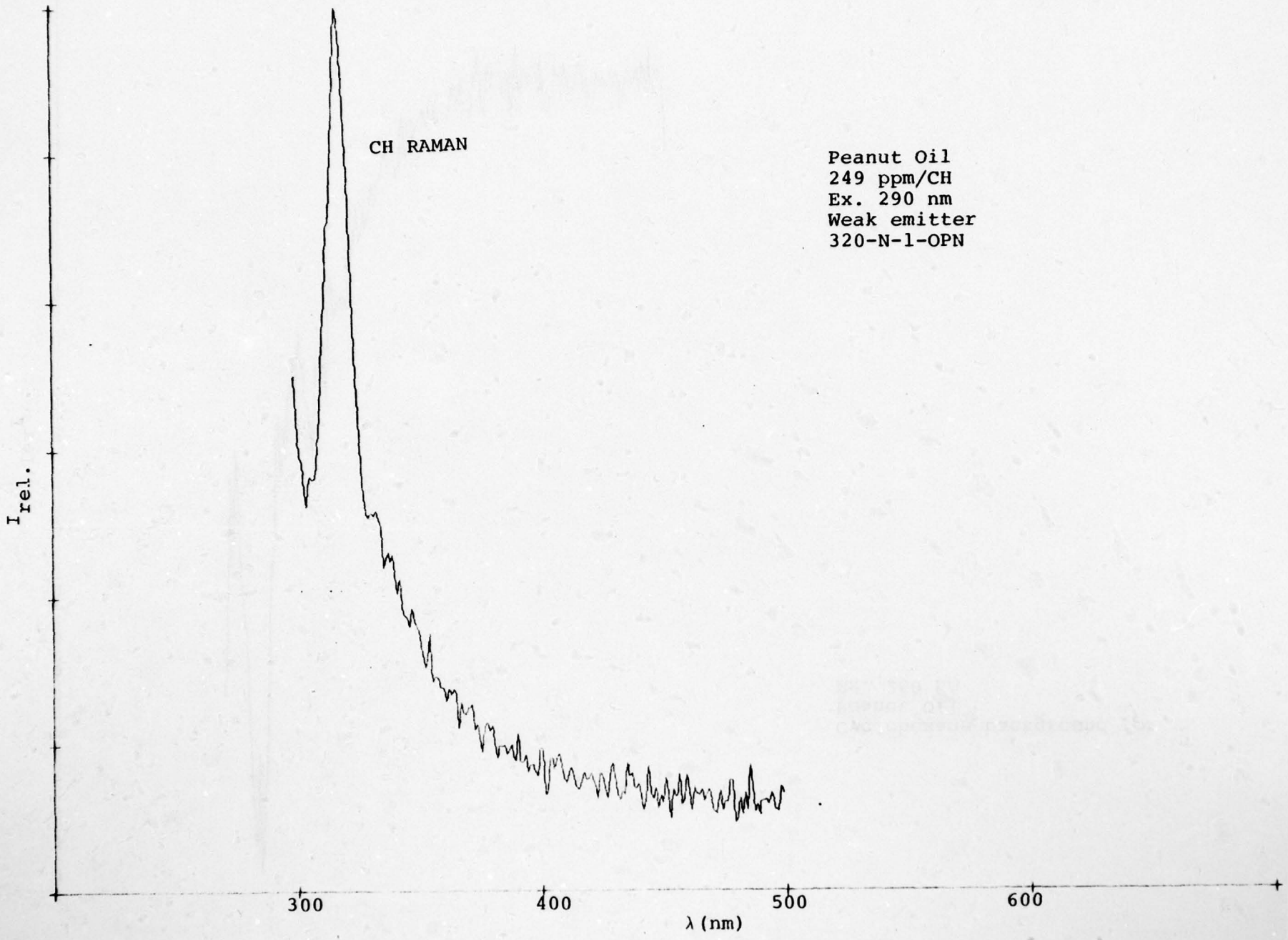


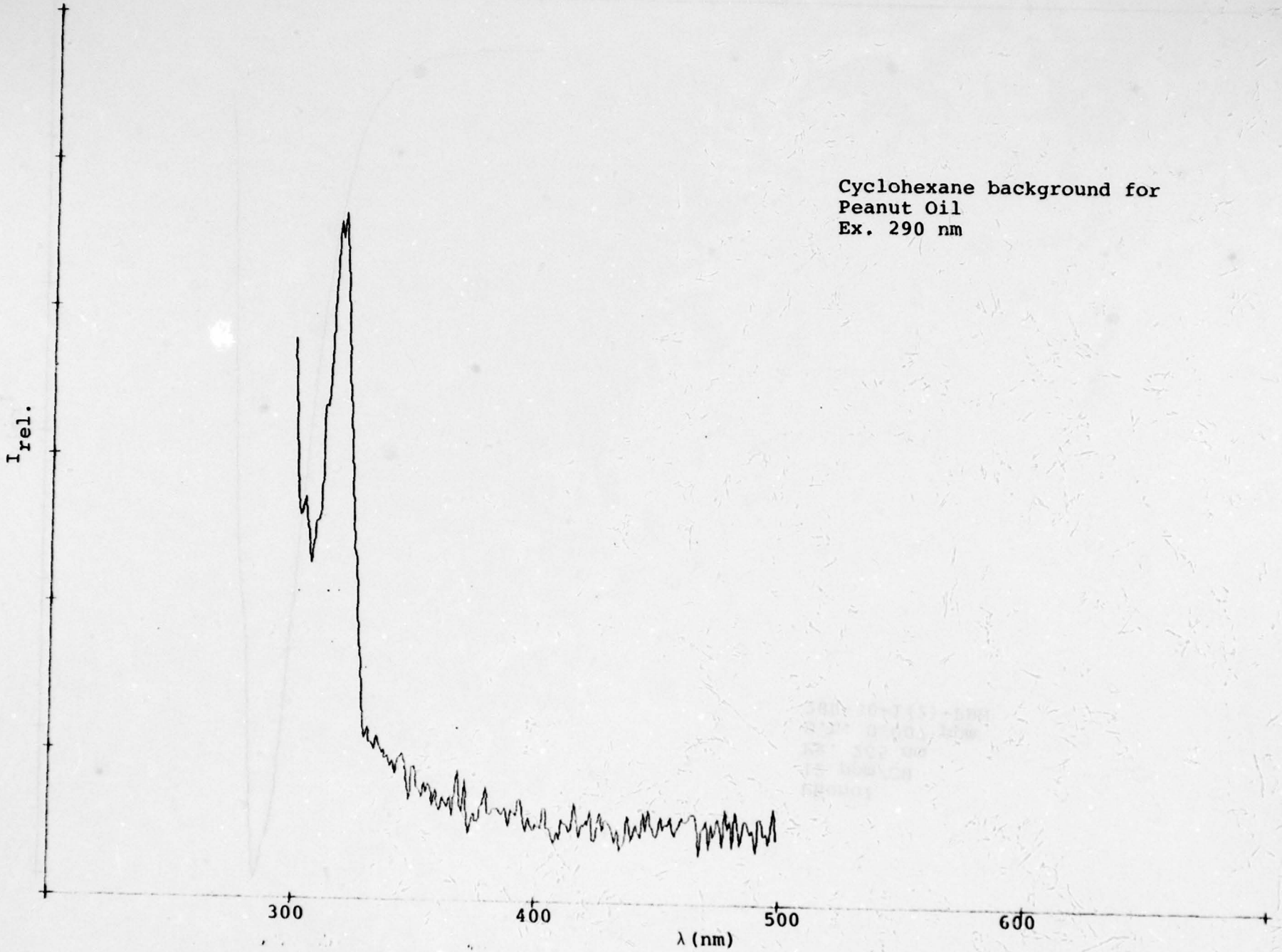
Cyclohexane background
for Parathion


Peanut Oil
249 ppm/CH
Ex. 260 nm
Weak emitter
320-N-1-OPN
$I_{rel.}$
300
400
λ (nm)
500
600

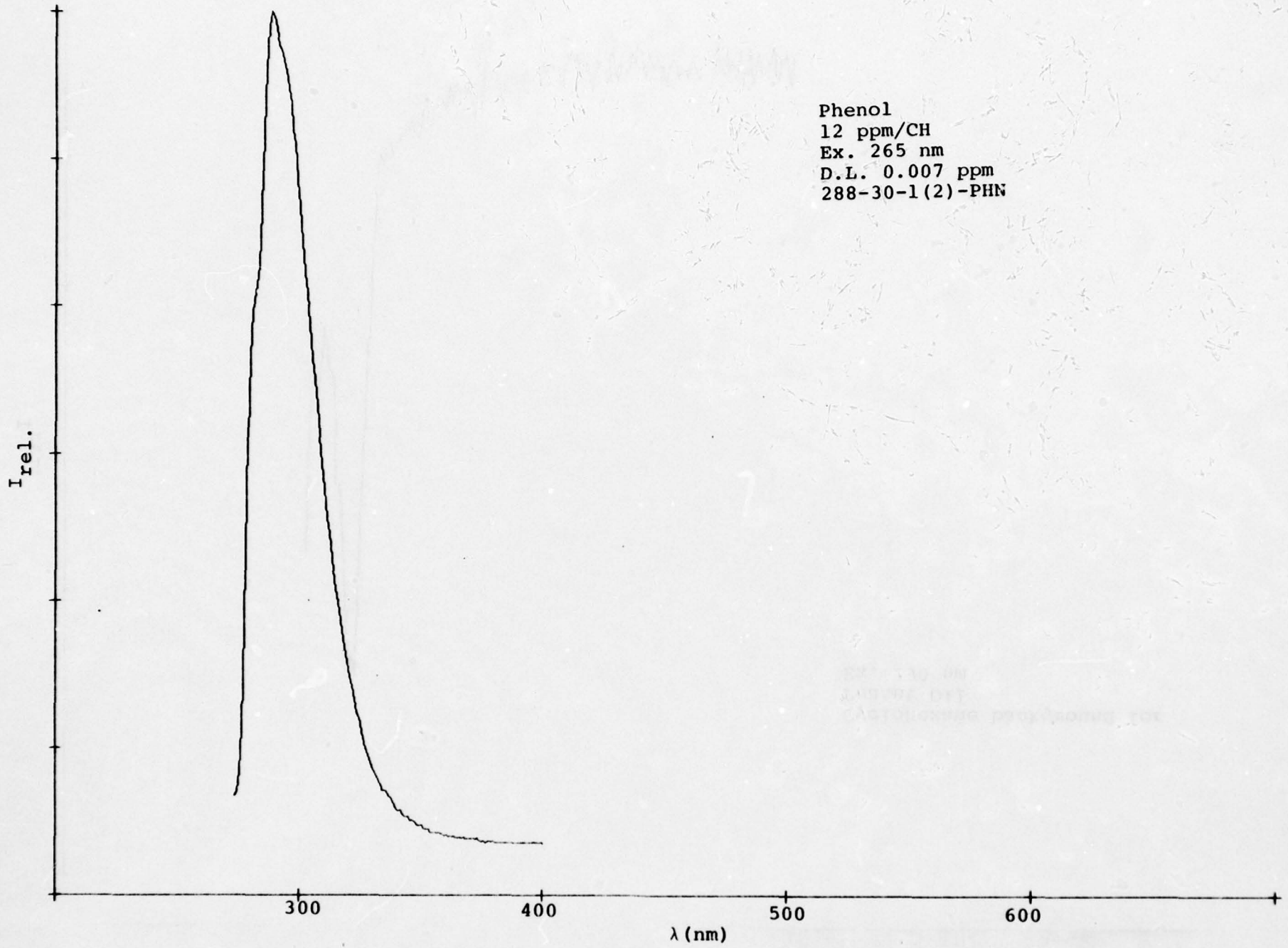


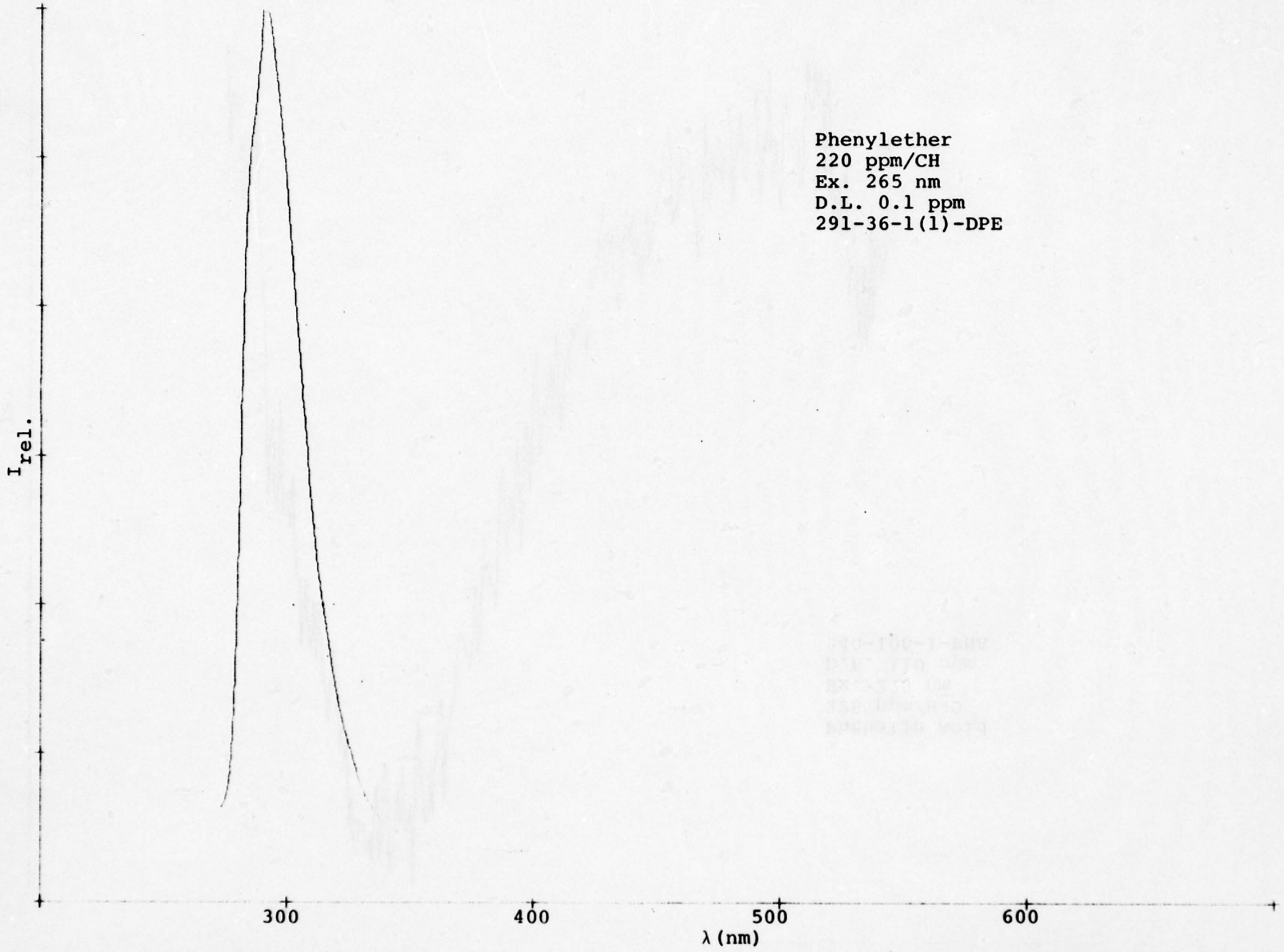
Cyclohexane background for
Peanut Oil
Ex. 260 nm

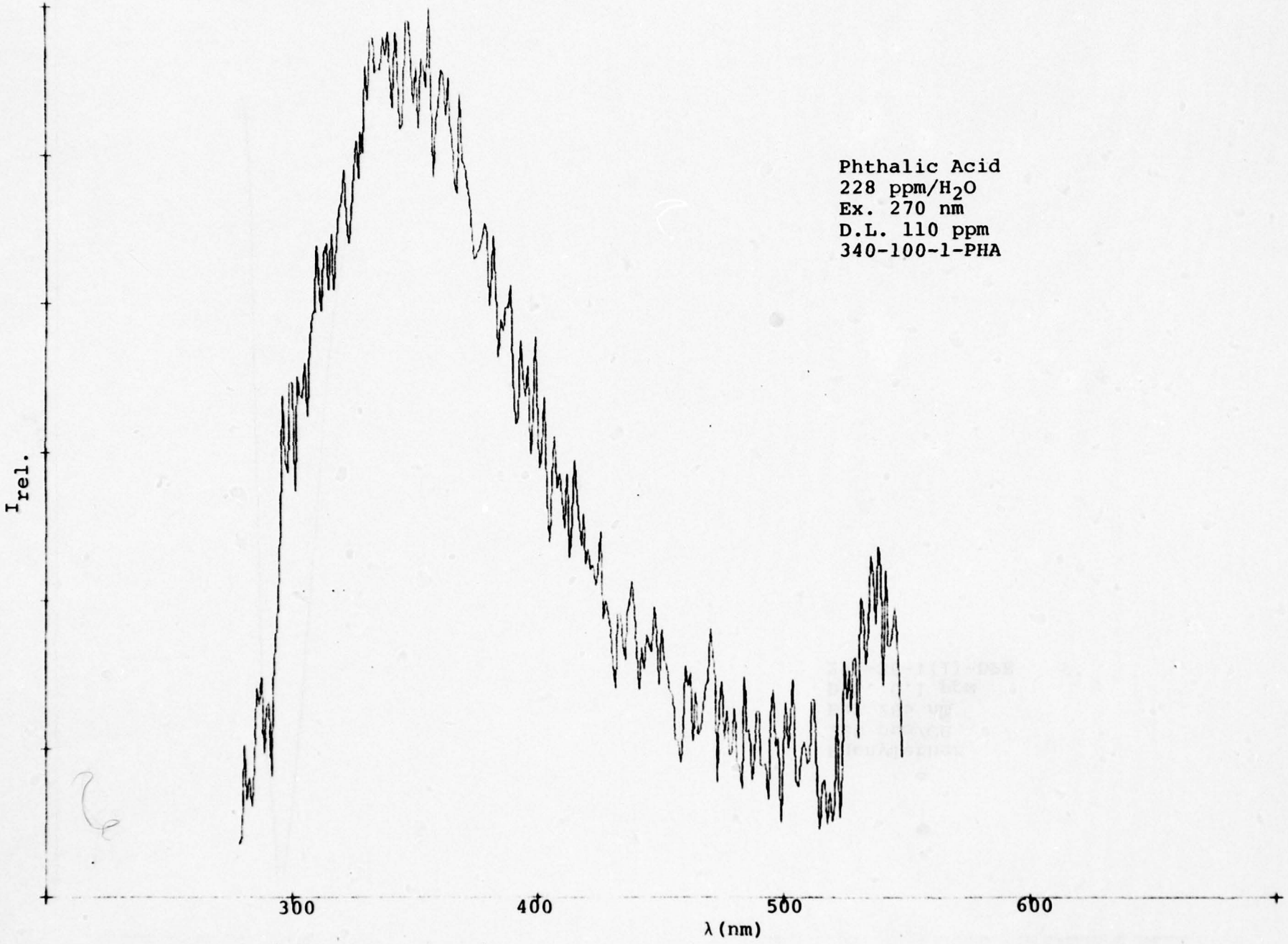

CH RAMAN
Peanut Oil
249 ppm/CH
Ex. 290 nm
Weak emitter
320-N-1-OPN
I rel.
300
400
500
600
λ (nm)

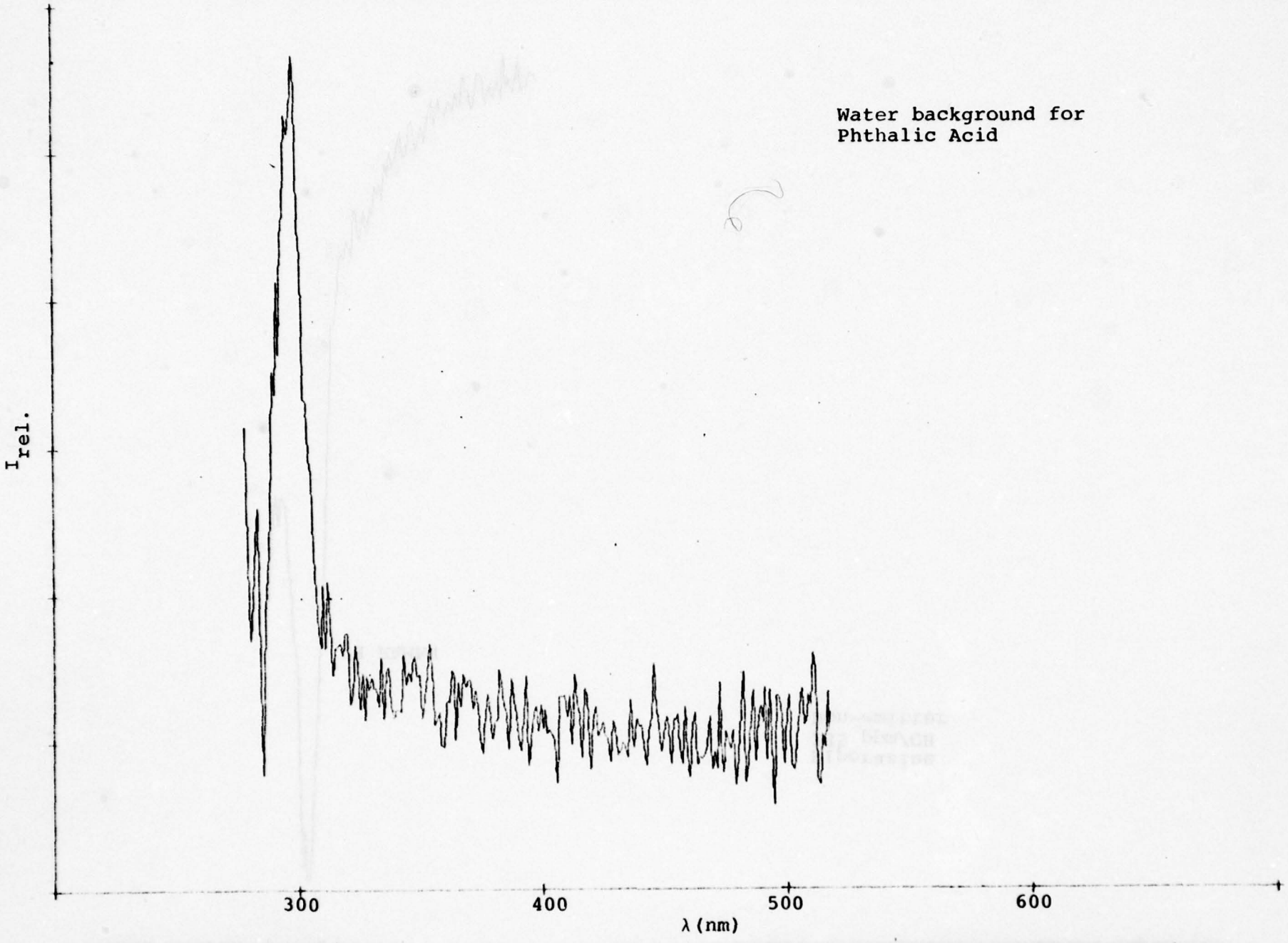


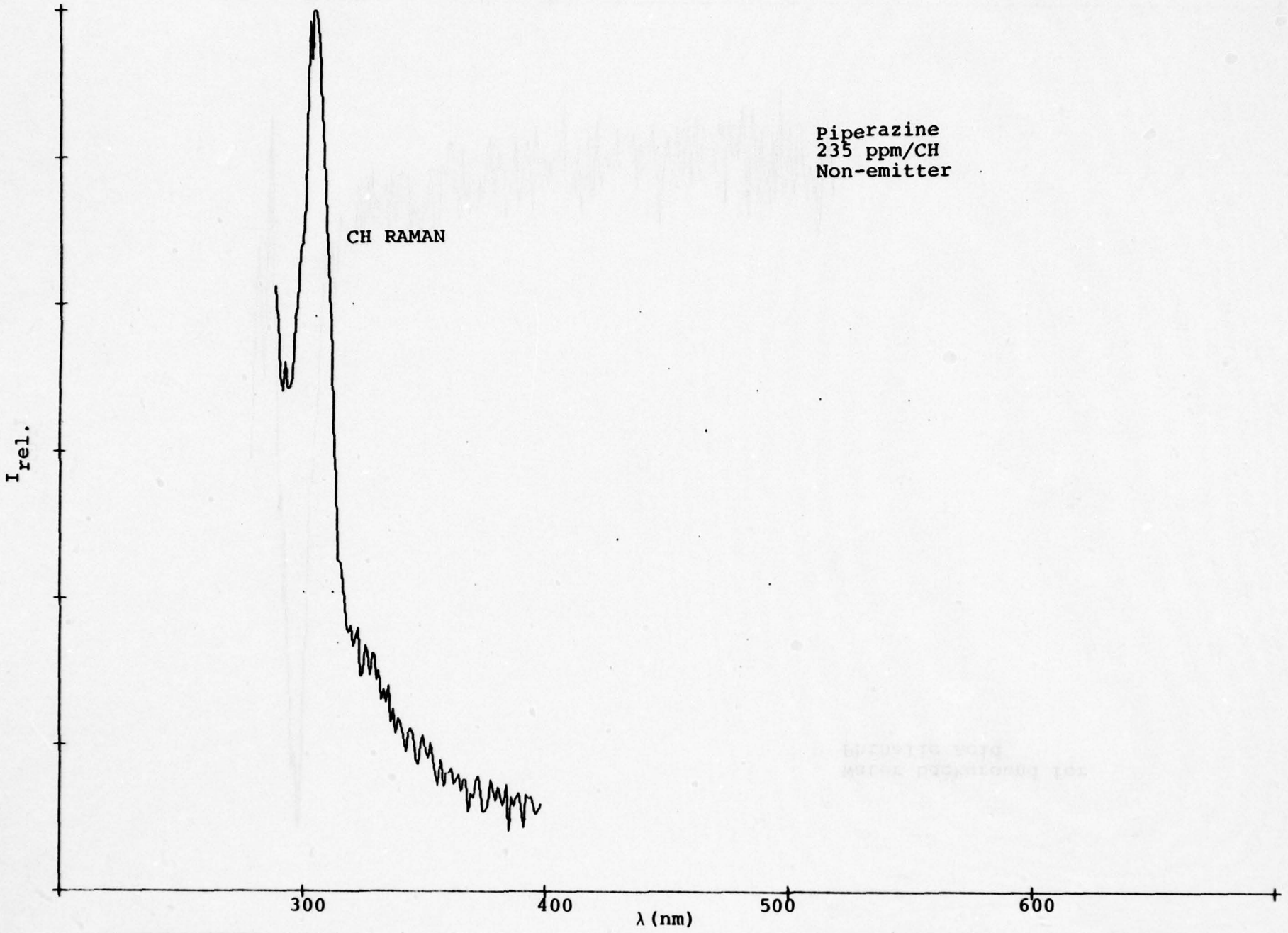
Cyclohexane background for
Peanut Oil
Ex. 290 nm

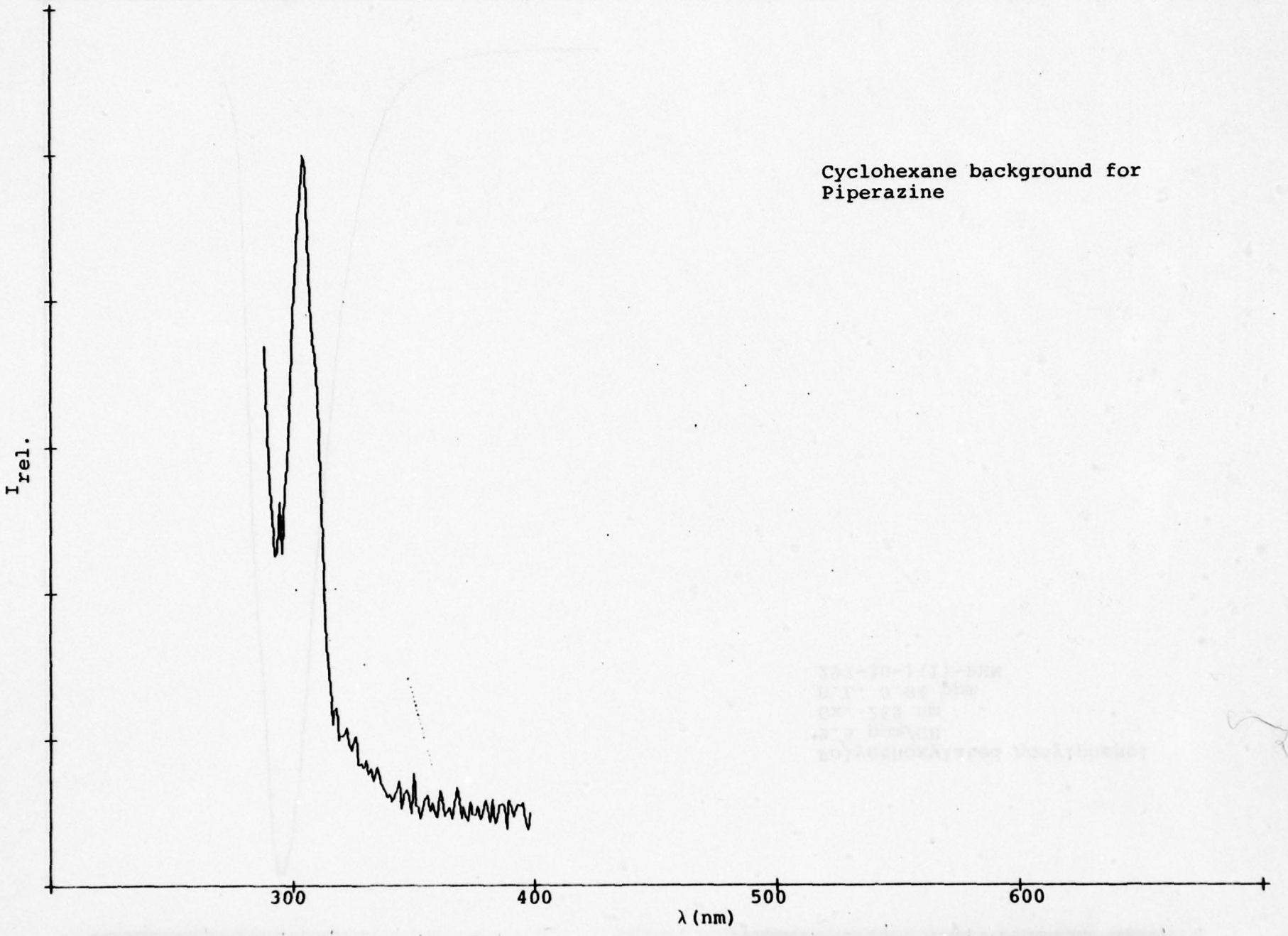

Phenol
12 ppm/CH
Ex. 265 nm
D.L. 0.007 ppm
288-30-1(2)-PHN
$I_{rel.}$
300
400
500
600
λ (nm)

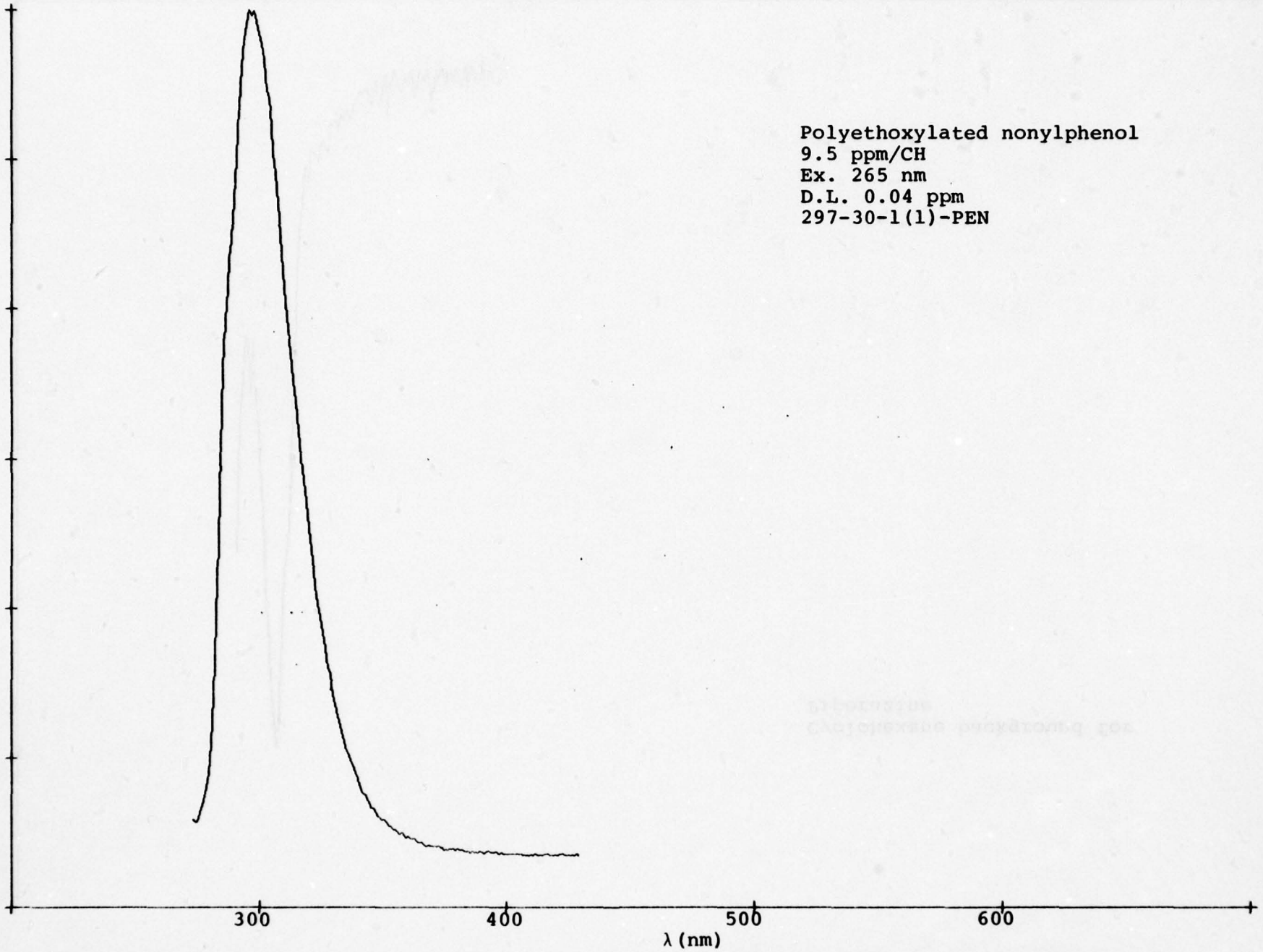

Phenylether
220 ppm/CH
Ex. 265 nm
D.L. 0.1 ppm
291-36-1(1)-DPE
$I_{rel.}$
300
400
500
600
λ (nm)

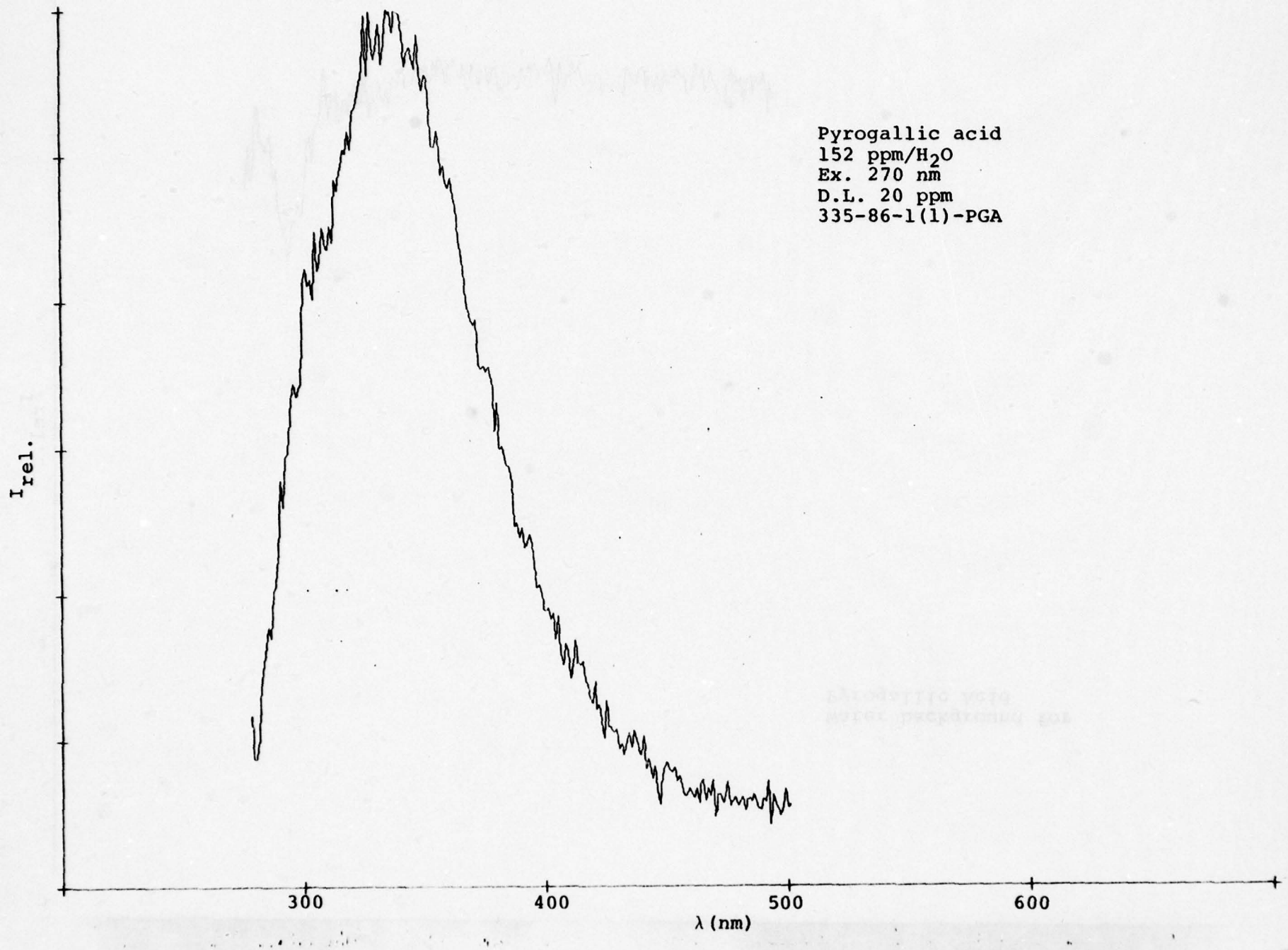

Phthalic Acid
228 ppm/H_2O
Ex. 270 nm
D.L. 110 ppm
340-100-1-PHA
$I_{rel.}$
300
400
500
600
λ (nm)


Water background for
Phthalic Acid
$I_{rel.}$
300
400
500
600
λ (nm)

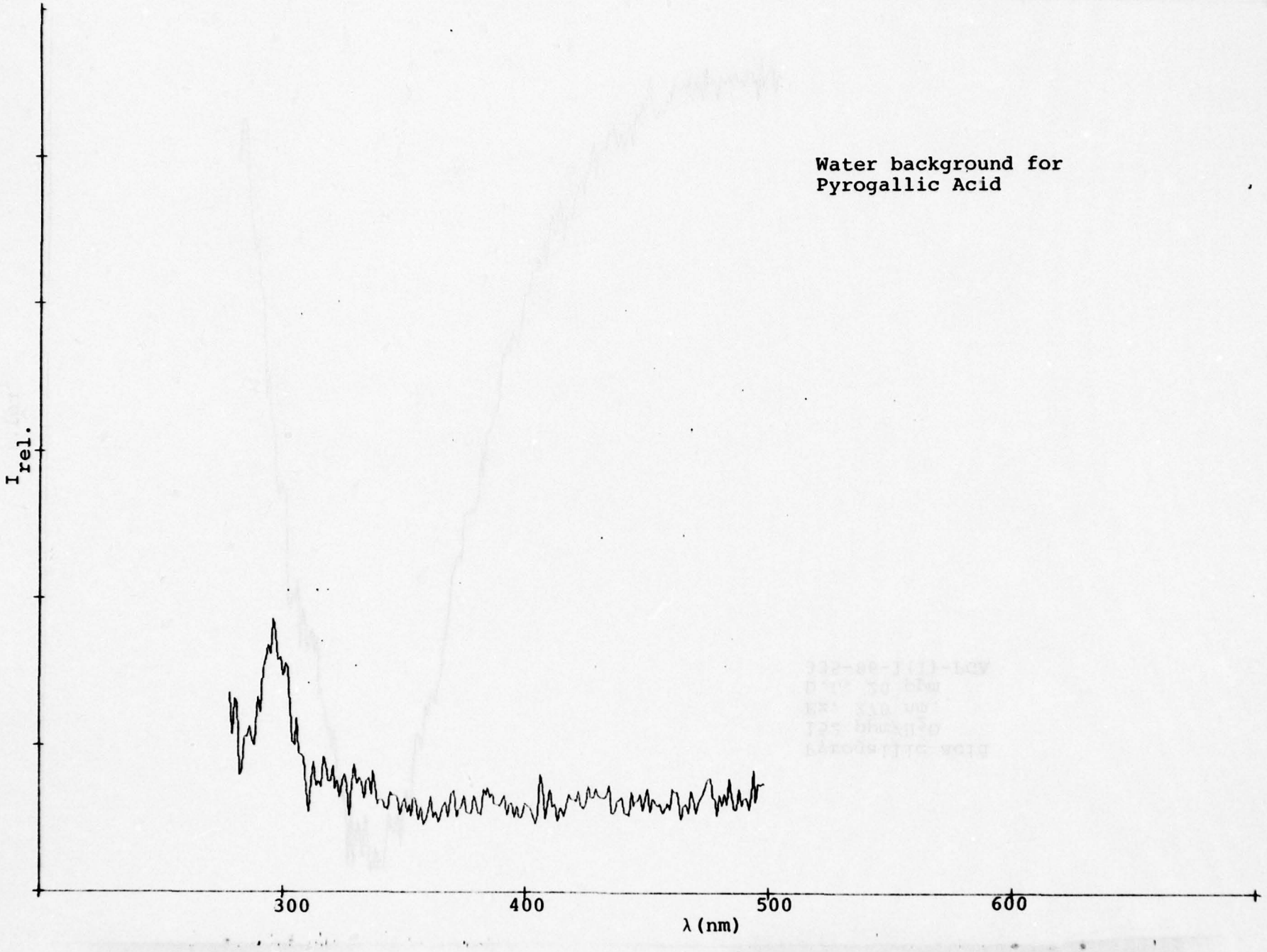

Piperazine
235 ppm/CH
Non-emitter
CH RAMAN
$I_{rel.}$
300
400
500
600
λ (nm)

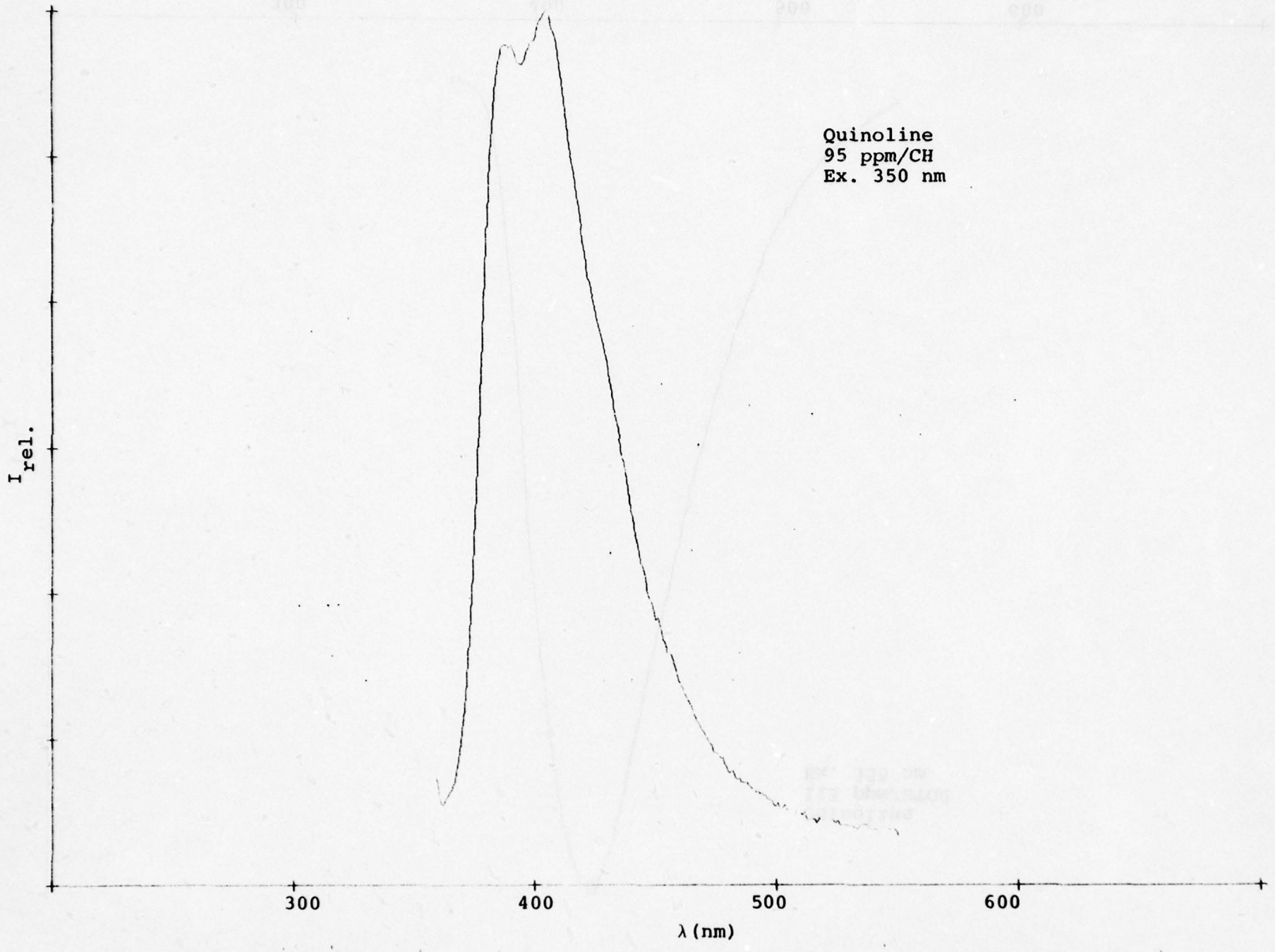

Cyclohexane background for
Piperazine
$I_{rel.}$
300
400
500
600
λ (nm)

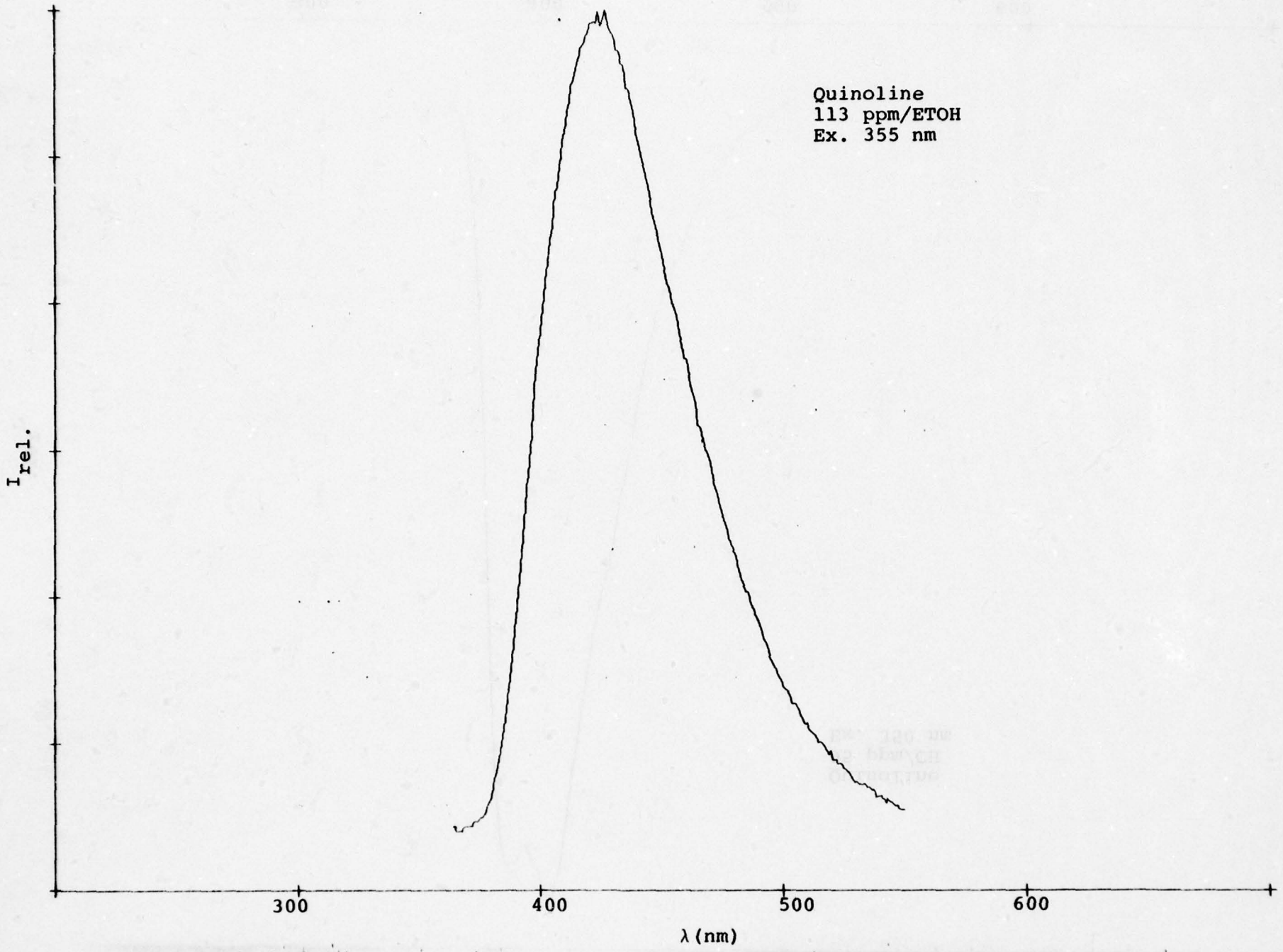

Polyethoxylated nonylphenol
9.5 ppm/CH
Ex. 265 nm
D.L. 0.04 ppm
297-30-1(1)-PEN
300
400
500
600
λ (nm)

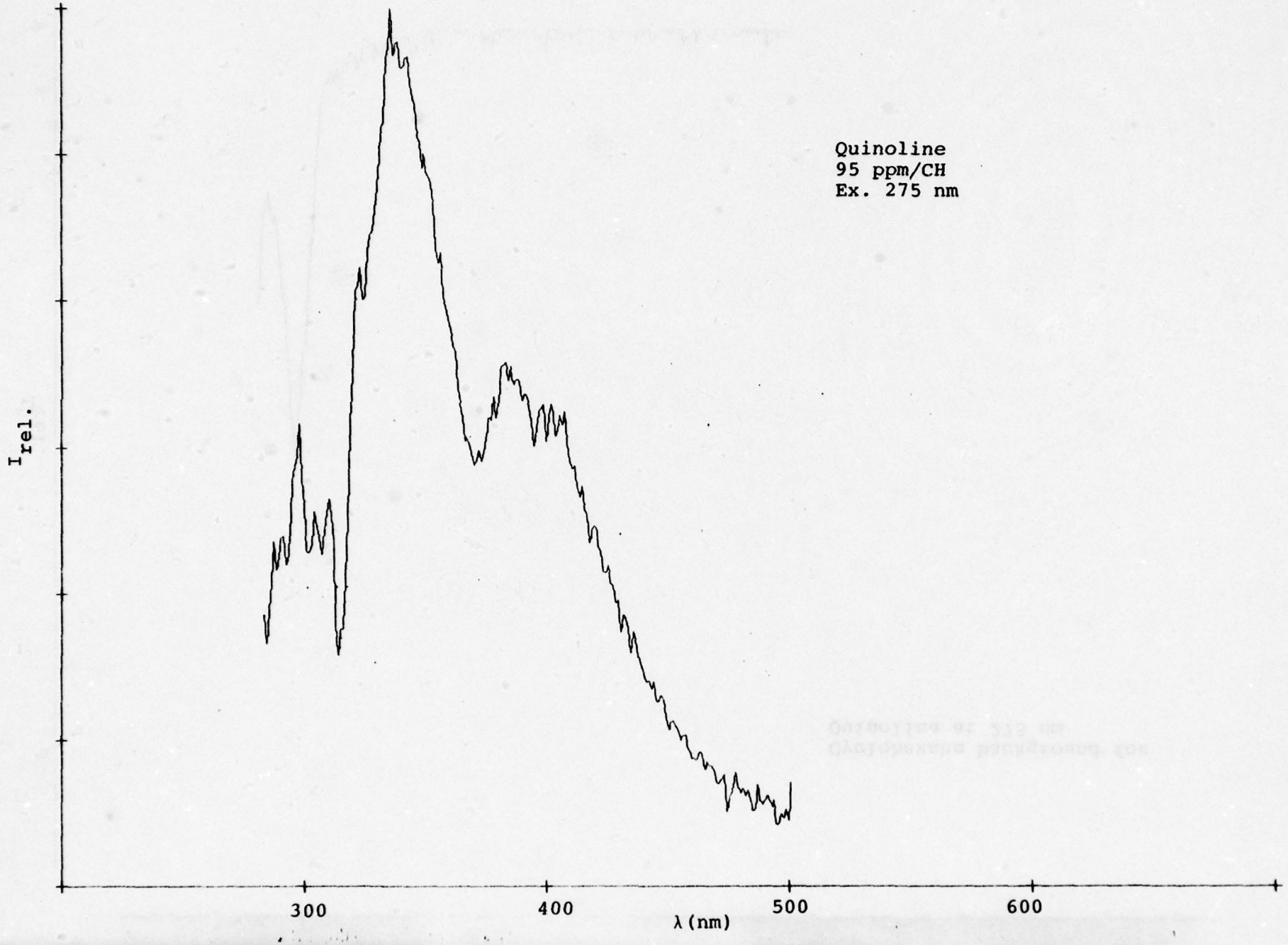

Pyrogallic acid
152 ppm/H_2O
Ex. 270 nm
D.L. 20 ppm
335-86-1(1)-PGA
$I_{rel.}$
300
400
500
600
λ (nm)

Water background for
Pyrogallic Acid

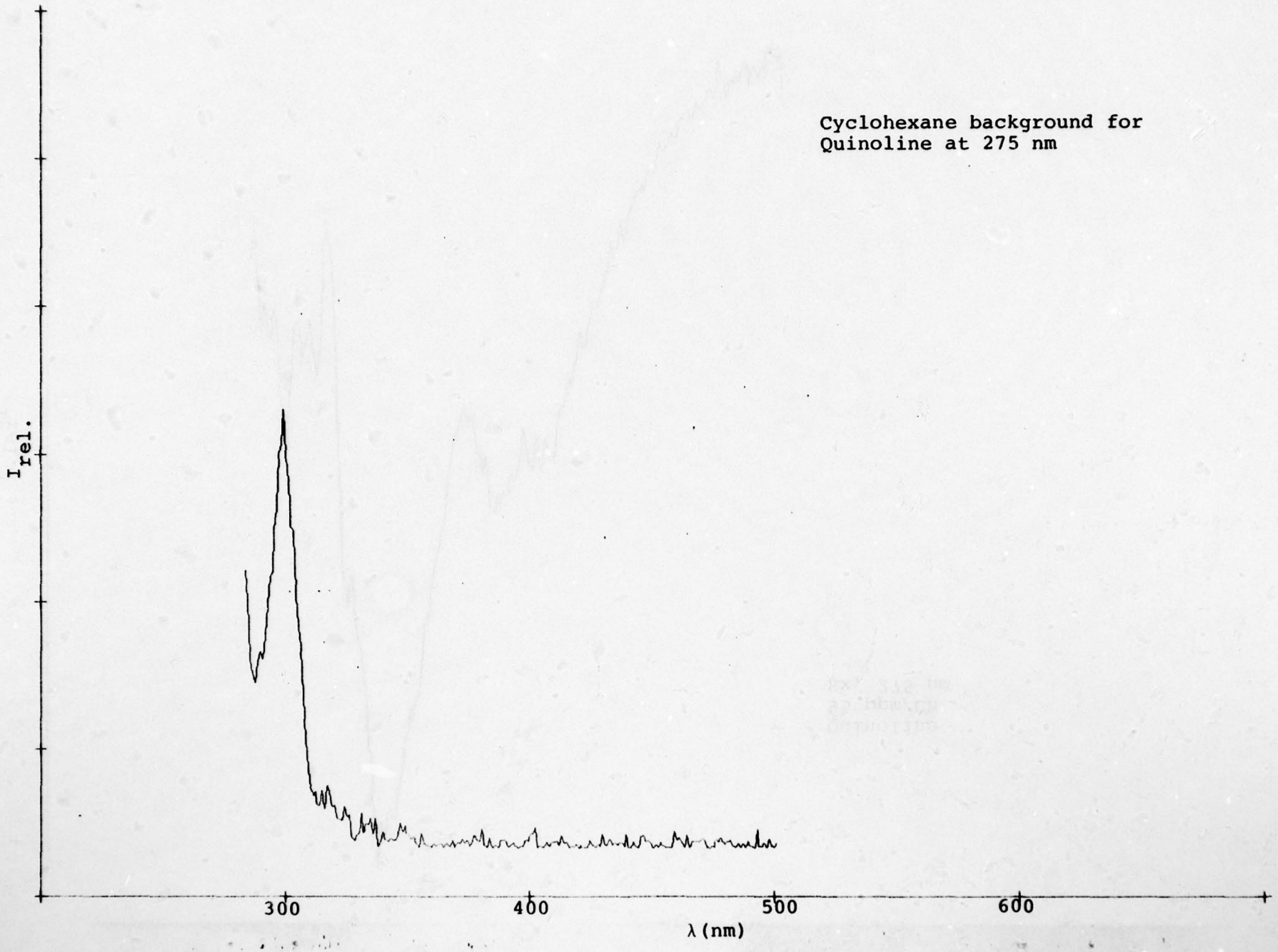


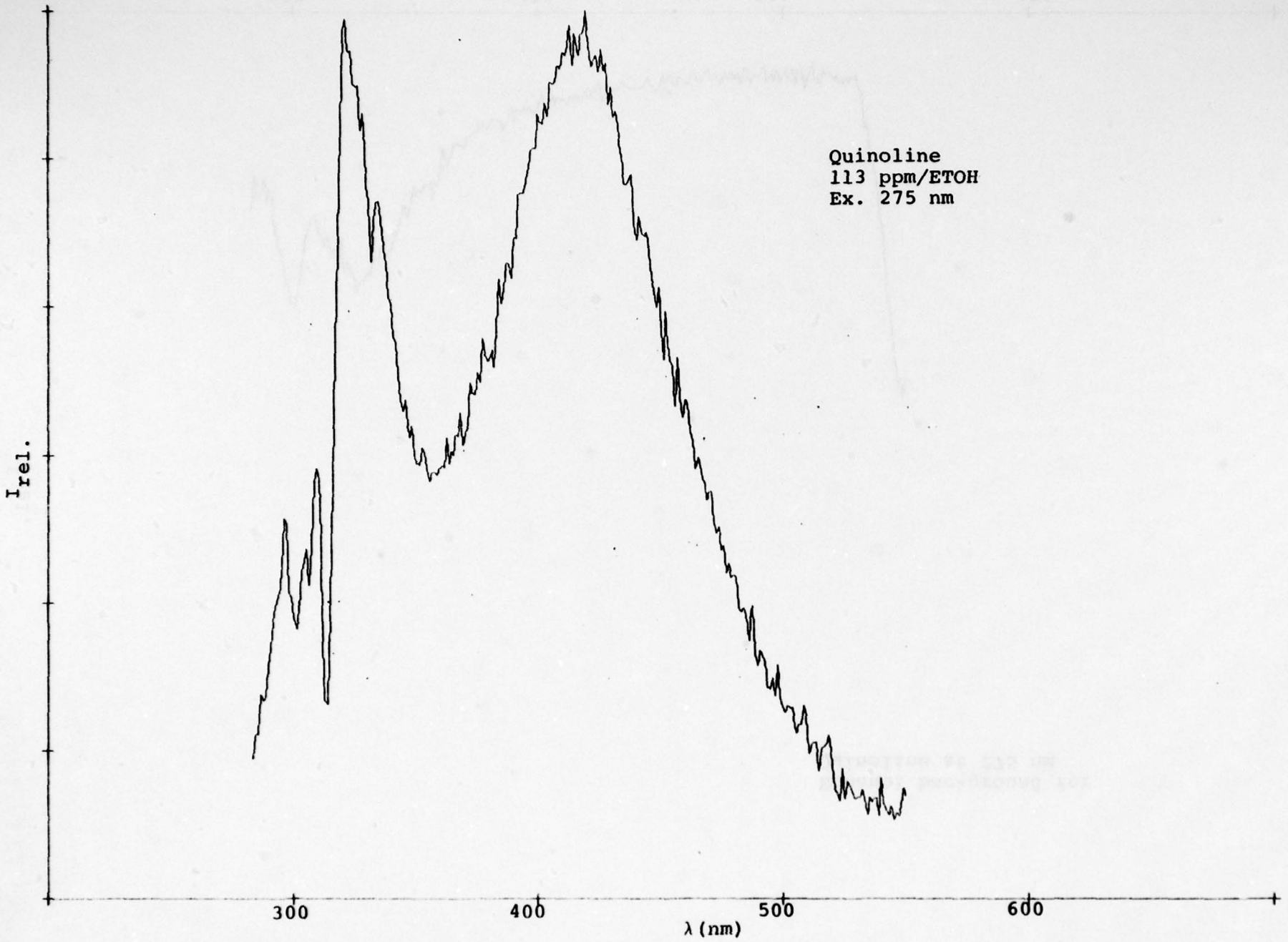

Quinoline
95 ppm/CH
Ex. 350 nm
$I_{rel.}$
300
400
500
600
λ (nm)

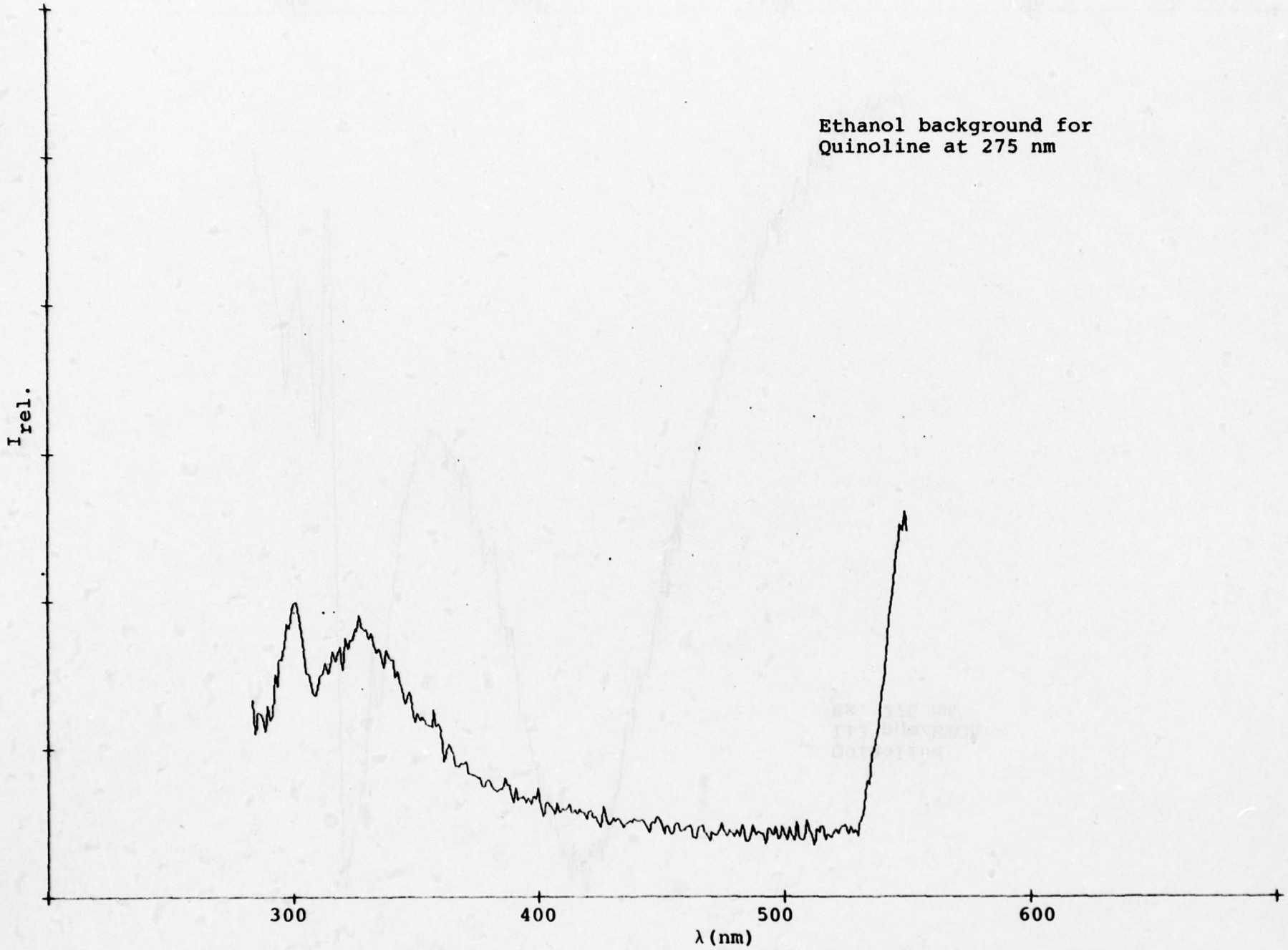

Quinoline
113 ppm/ETOH
Ex. 355 nm
$I_{rel.}$
300
400
500
600
λ (nm)

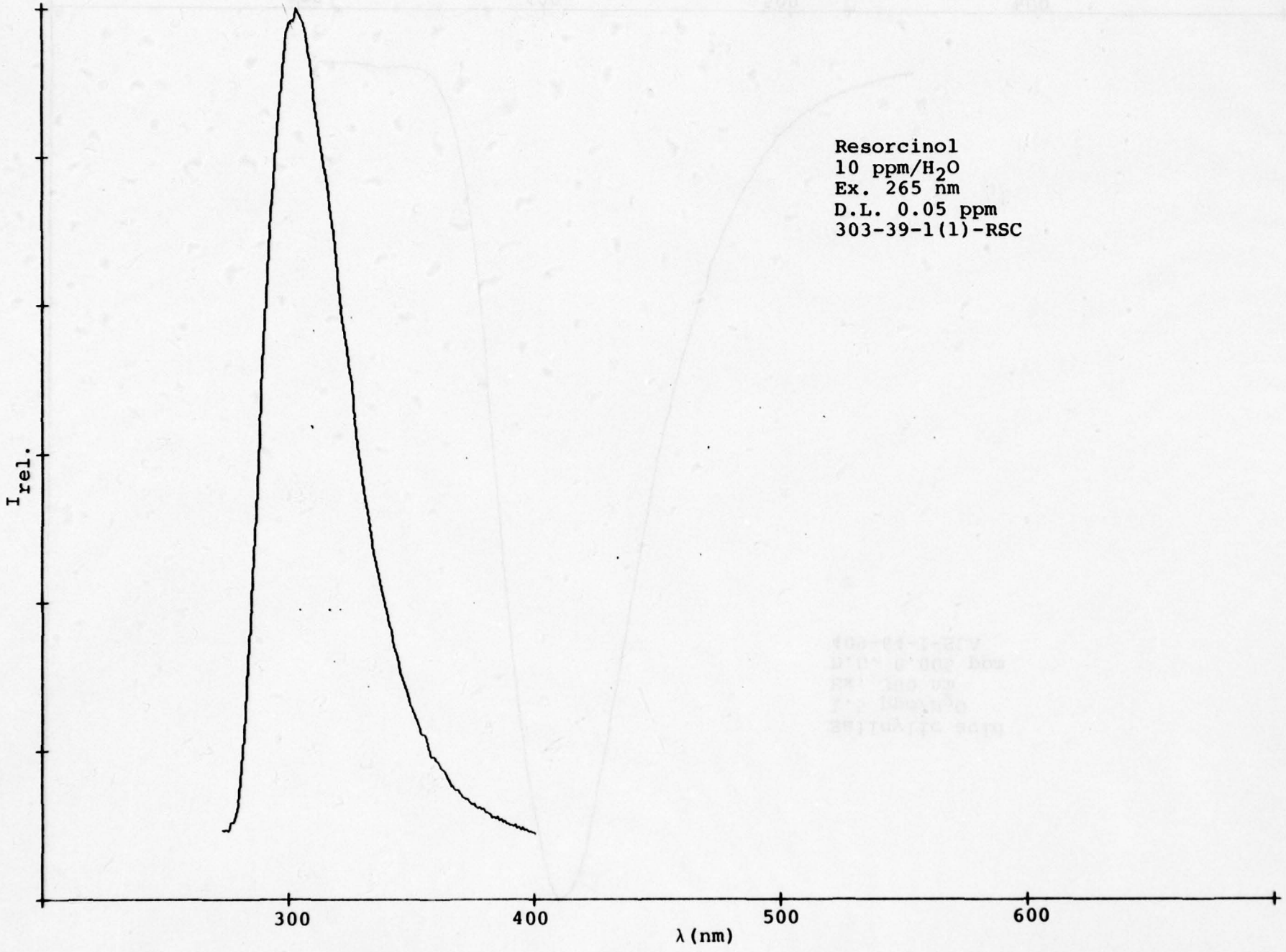

Quinoline
95 ppm/CH
Ex. 275 nm
$I_{rel.}$
300
400
500
600
λ (nm)

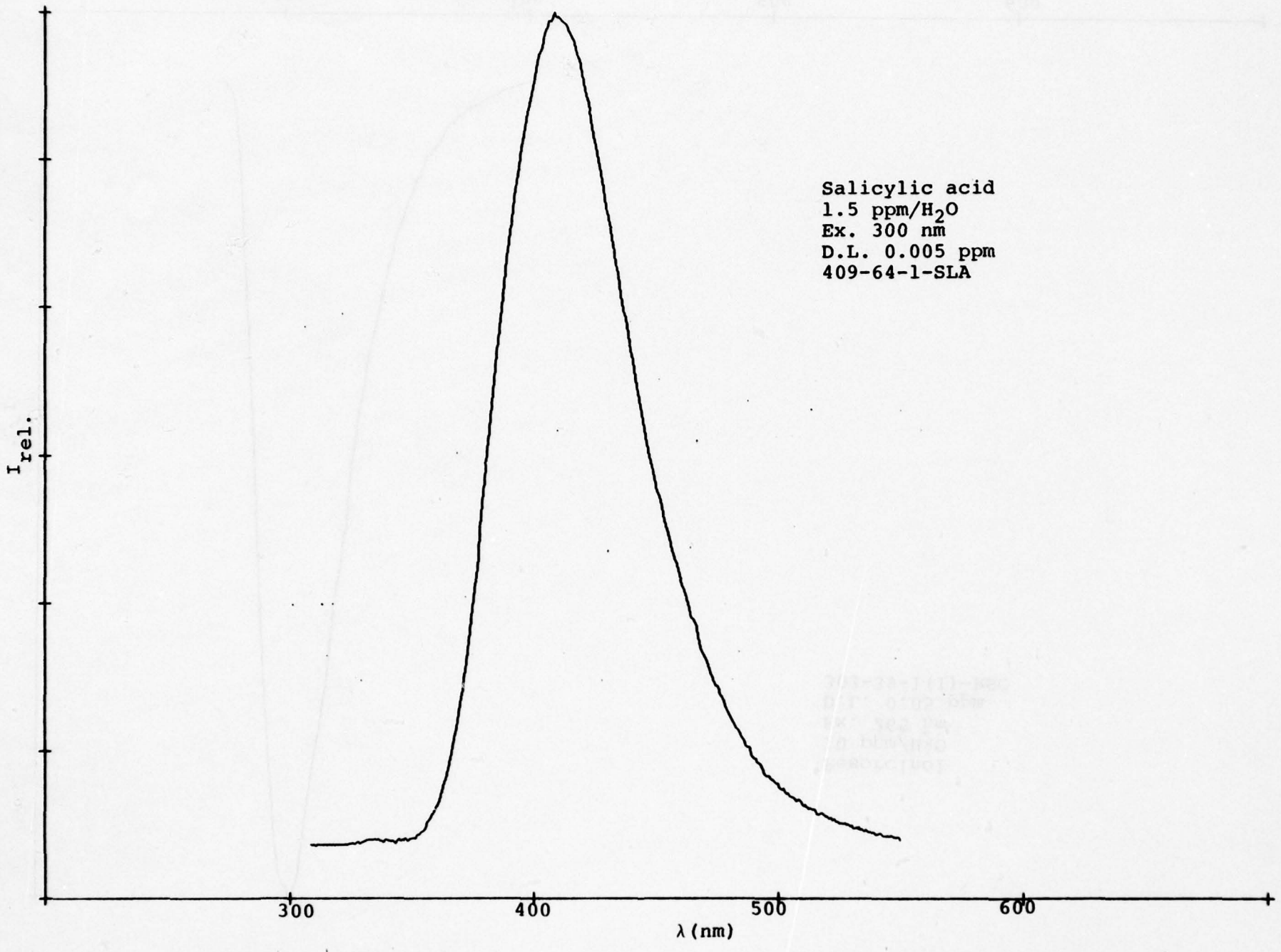
Cyclohexane background for
Quinoline at 275 nm

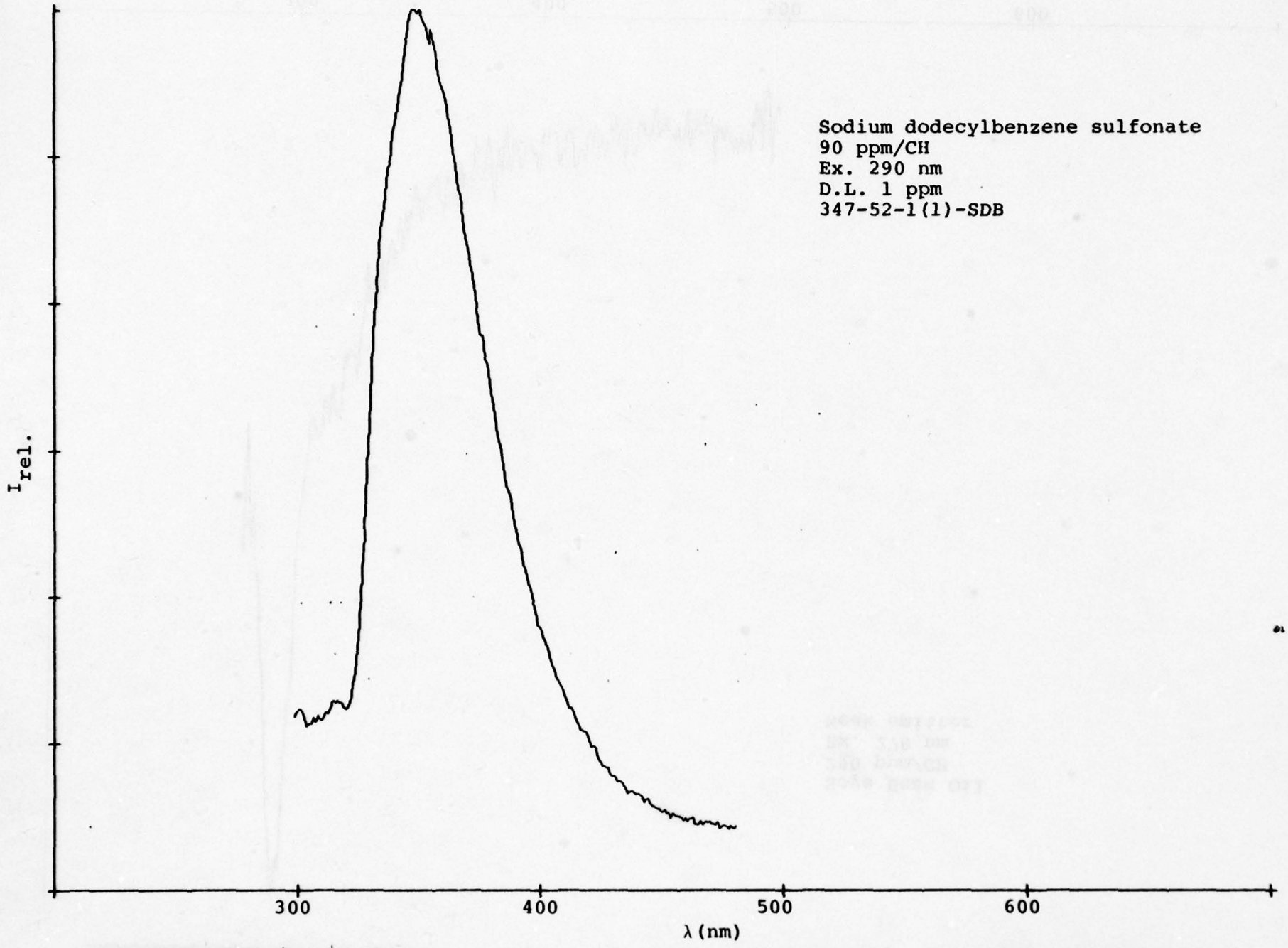


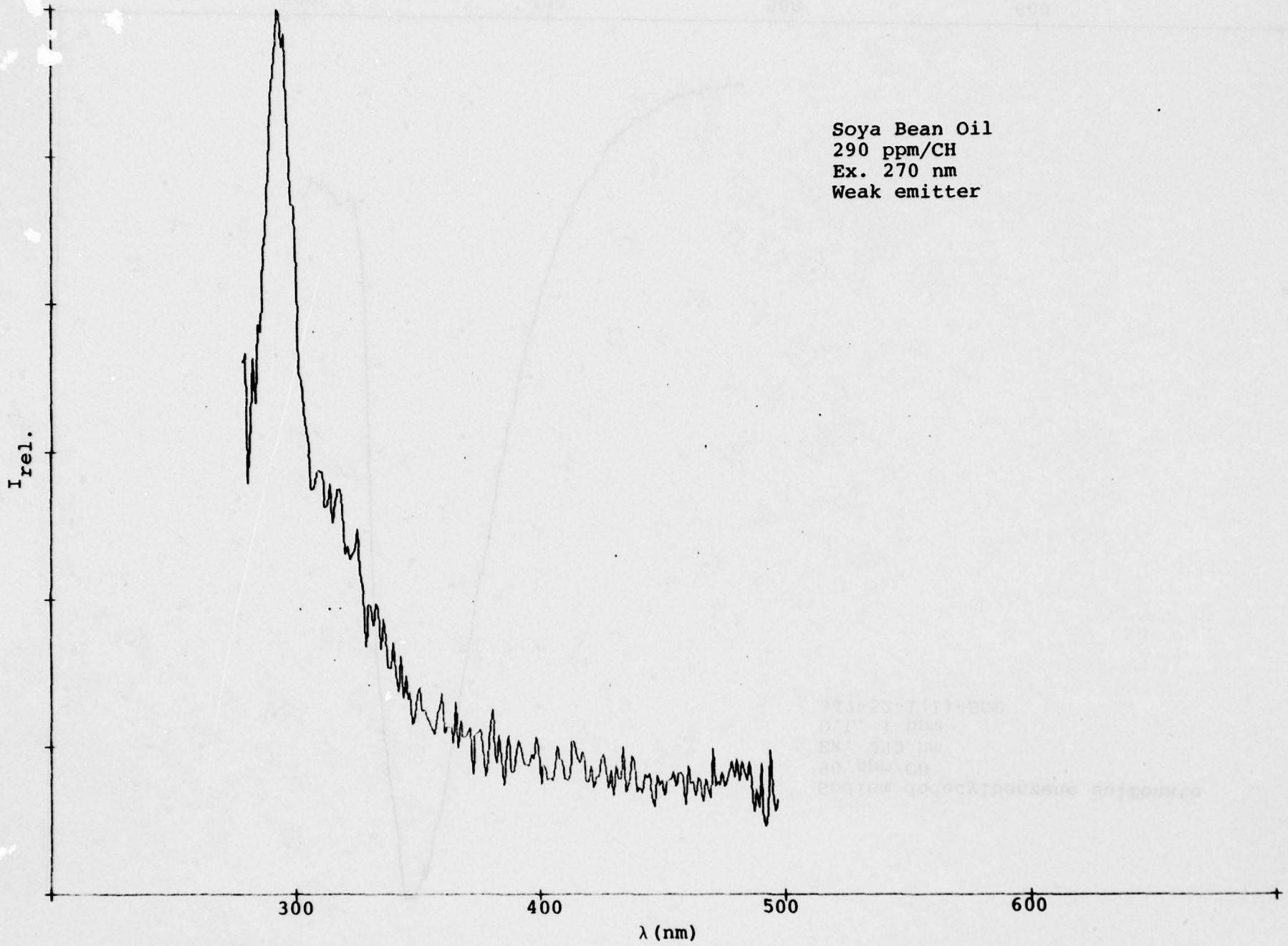

Quinoline
113 ppm/ETOH
Ex. 275 nm
$I_{rel.}$
300
400
500
600
λ (nm)

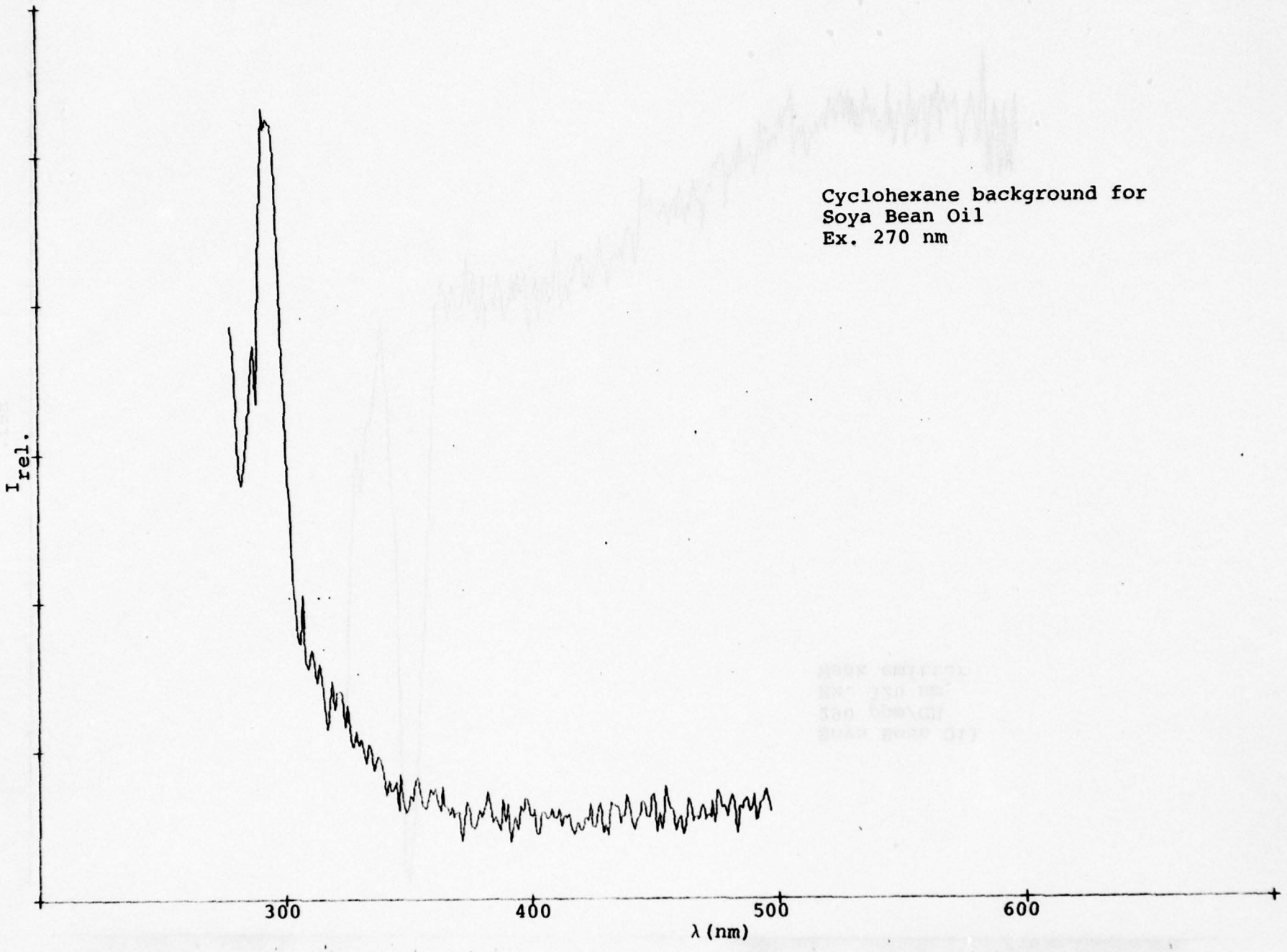

Ethanol background for
Quinoline at 275 nm
$I_{rel.}$
300
400
500
600
λ (nm)

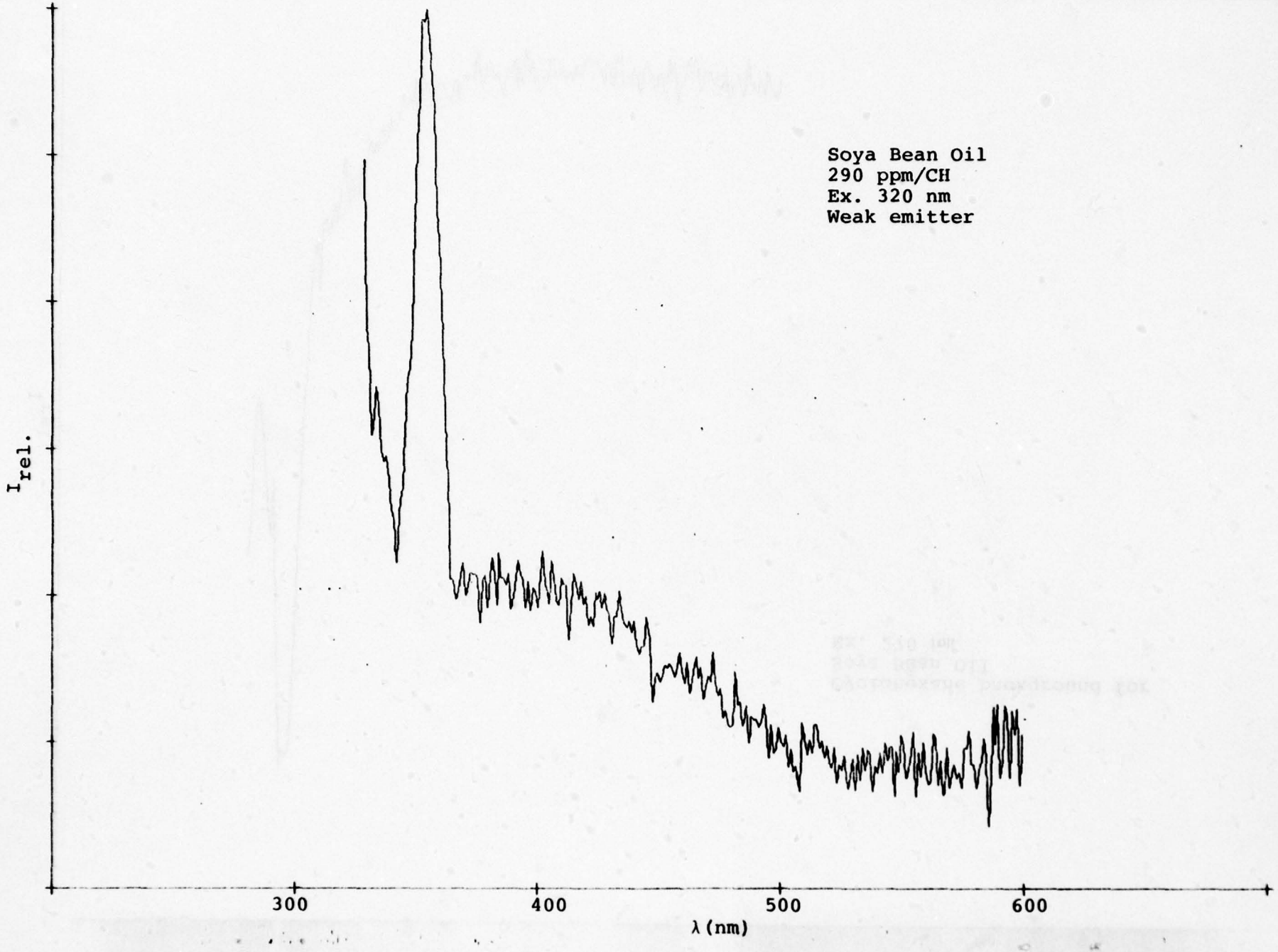

Resorcinol
10 ppm/H_2O
Ex. 265 nm
D.L. 0.05 ppm
303-39-1(1)-RSC
$I_{rel.}$
300
400
500
600
λ (nm)

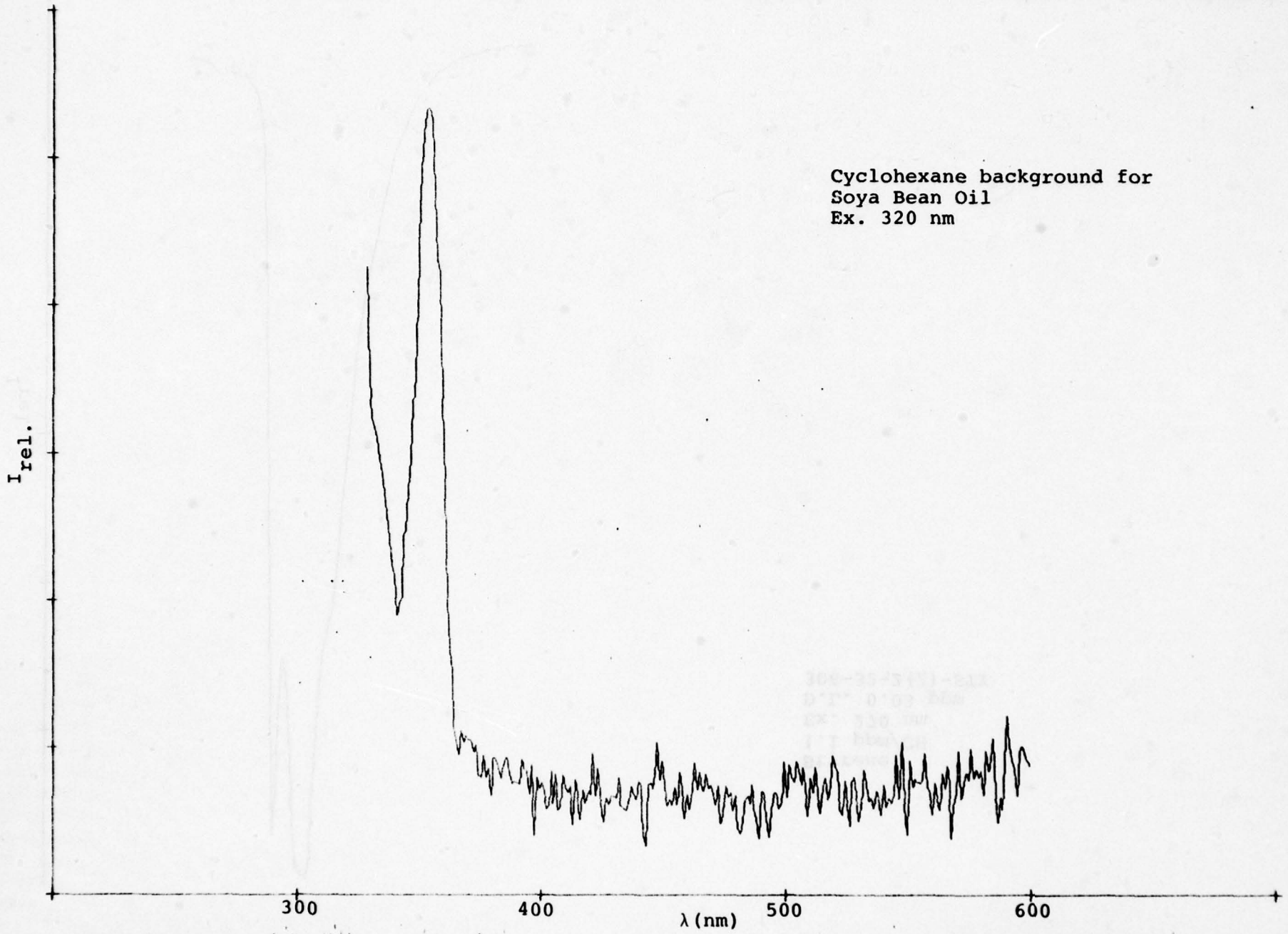

Salicylic acid
1.5 ppm/H_2O
Ex. 300 nm
D.L. 0.005 ppm
409-64-1-SLA
$I_{rel.}$
300
400
500
600
λ (nm)

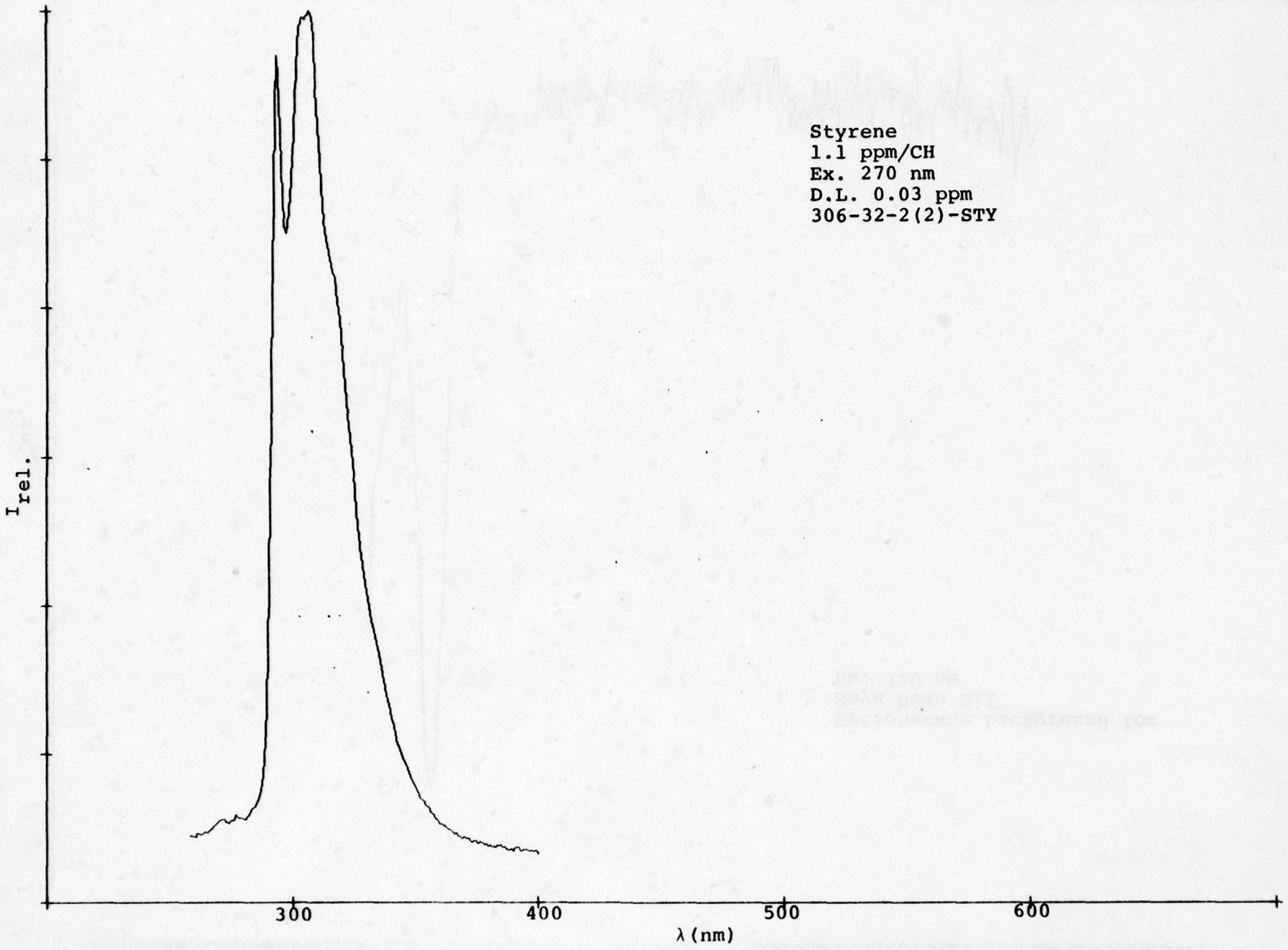

Sodium dodecylbenzene sulfonate
90 ppm/CH
Ex. 290 nm
D.L. 1 ppm
347-52-1(1)-SDB
$I_{rel.}$
300
400
500
600
λ (nm)

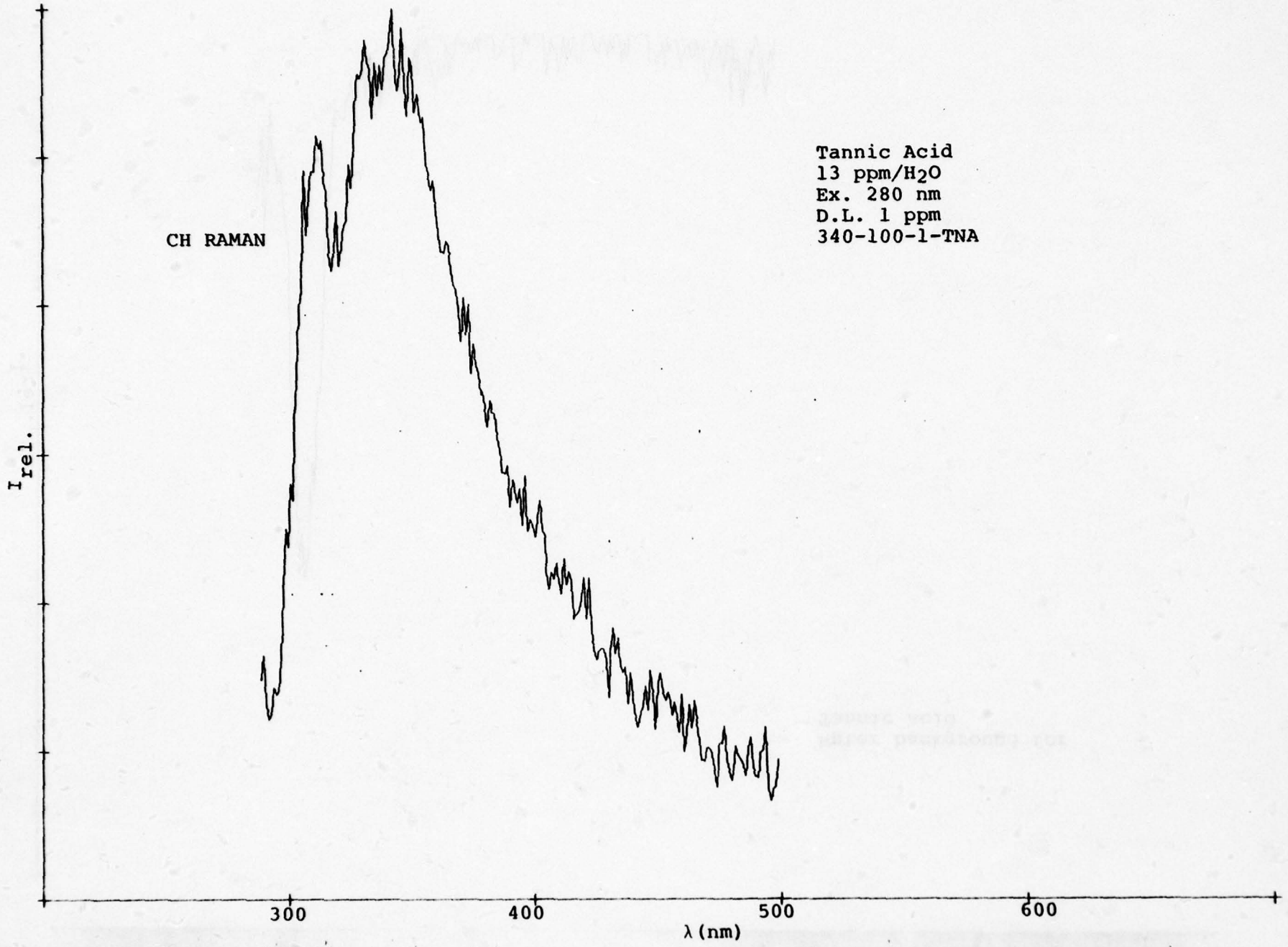

Soya Bean Oil
290 ppm/CH
Ex. 270 nm
Weak emitter
$I_{rel.}$
300
400
500
600
λ (nm)


Cyclohexane background for
Soya Bean Oil
Ex. 270 nm
I rel.
300
400
500
600
λ (nm)

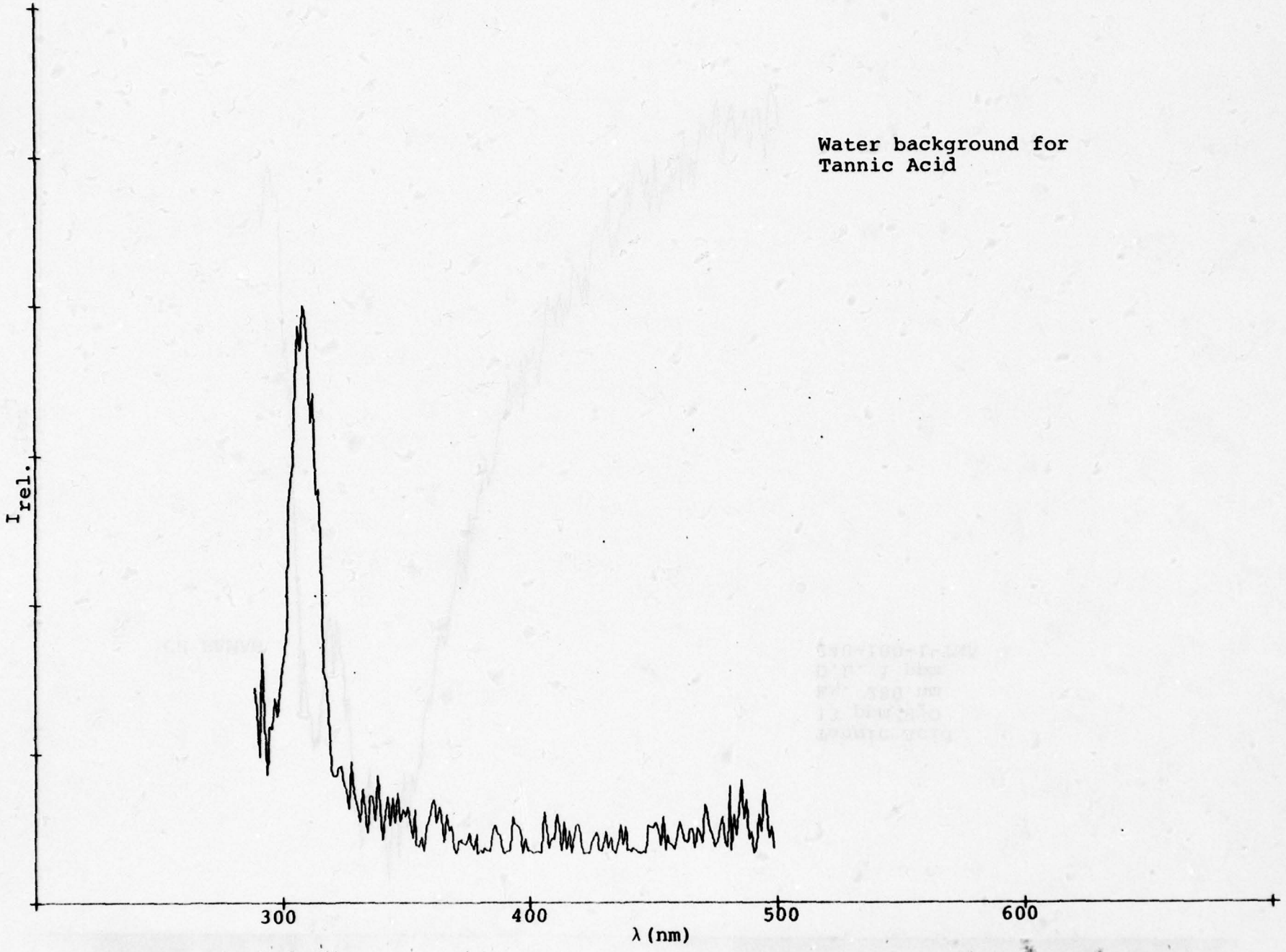

Soya Bean Oil
290 ppm/CH
Ex. 320 nm
Weak emitter
$I_{rel.}$
300
400
500
600
λ (nm)

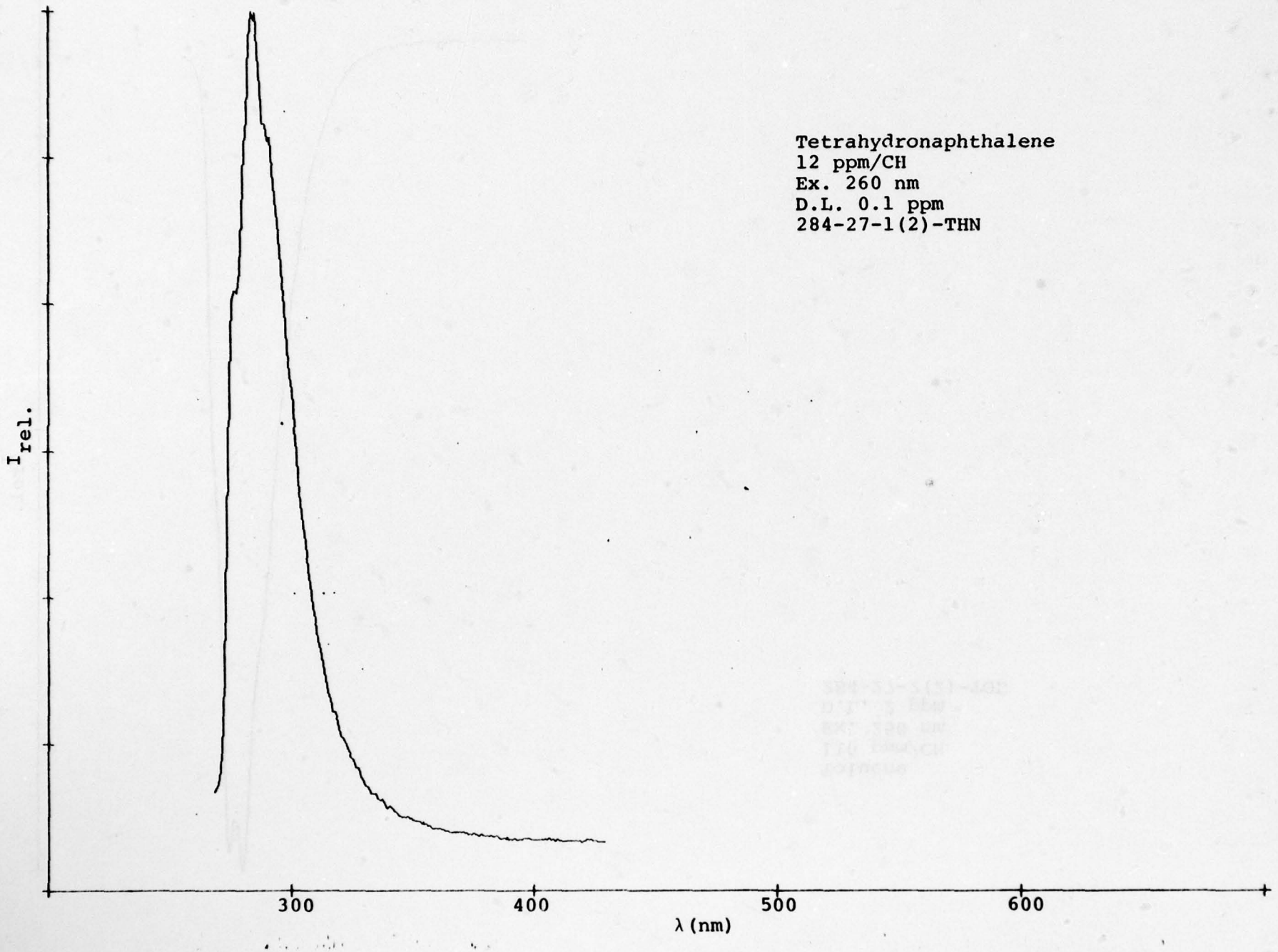

Cyclohexane background for
Soya Bean Oil
Ex. 320 nm
$I_{rel.}$
300
400
500
600
λ (nm)

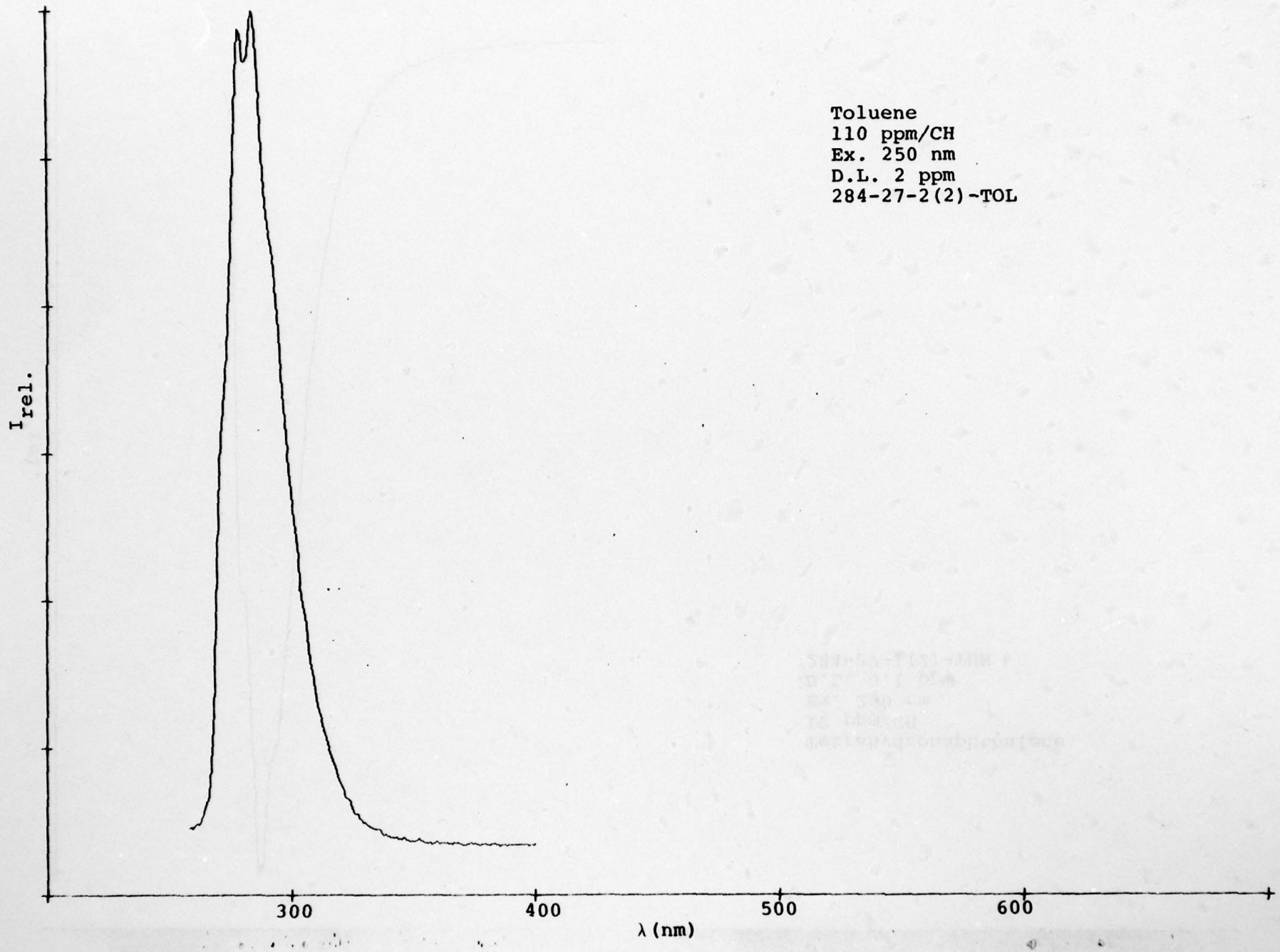

Styrene
1.1 ppm/CH
Ex. 270 nm
D.L. 0.03 ppm
306-32-2(2)-STY
$I_{rel.}$
300
400
500
600
λ (nm)

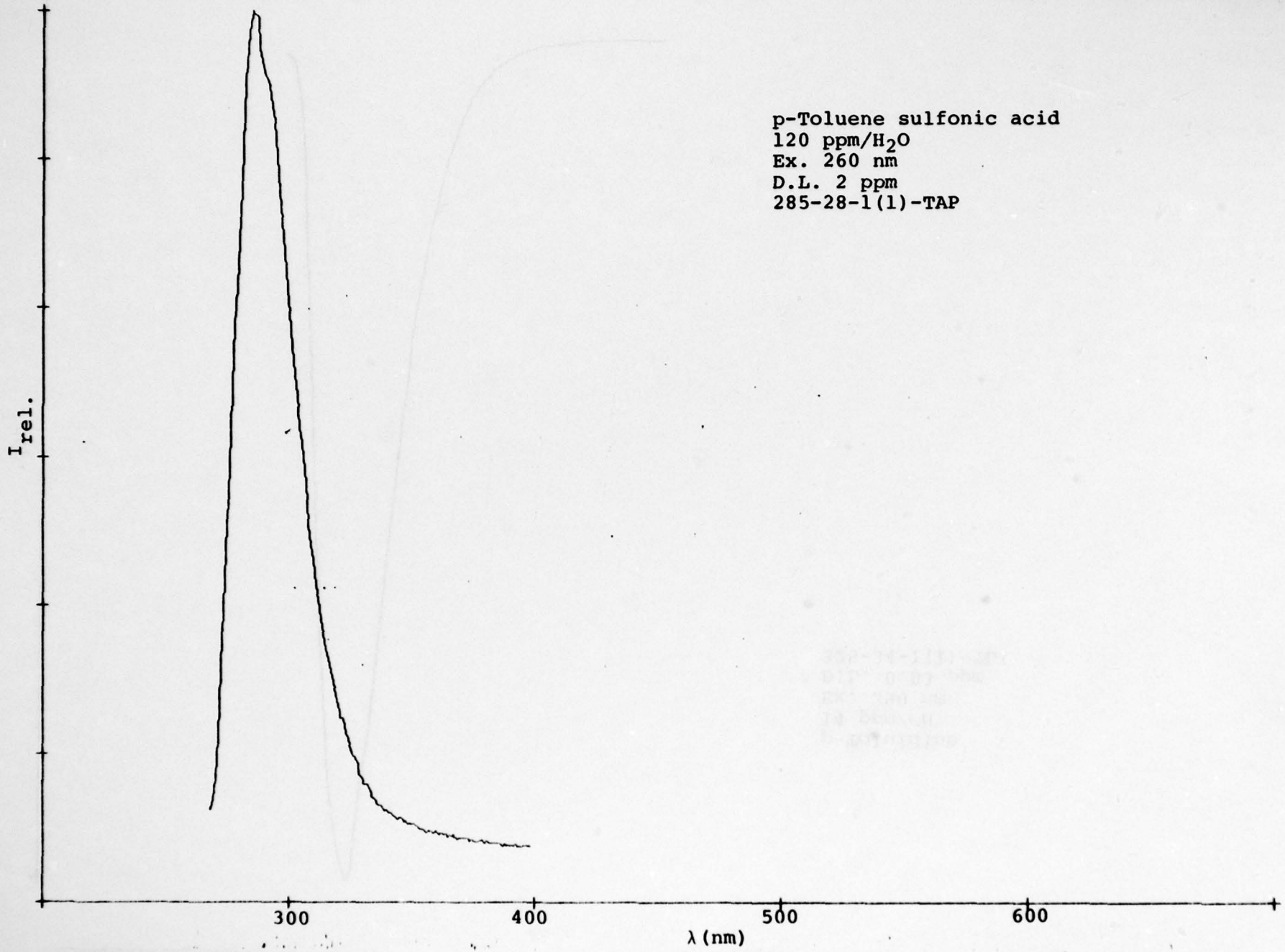

CH RAMAN
Tannic Acid
13 ppm/H_2O
Ex. 280 nm
D.L. 1 ppm
340-100-1-TNA
$I_{rel.}$
300
400
500
600
λ (nm)

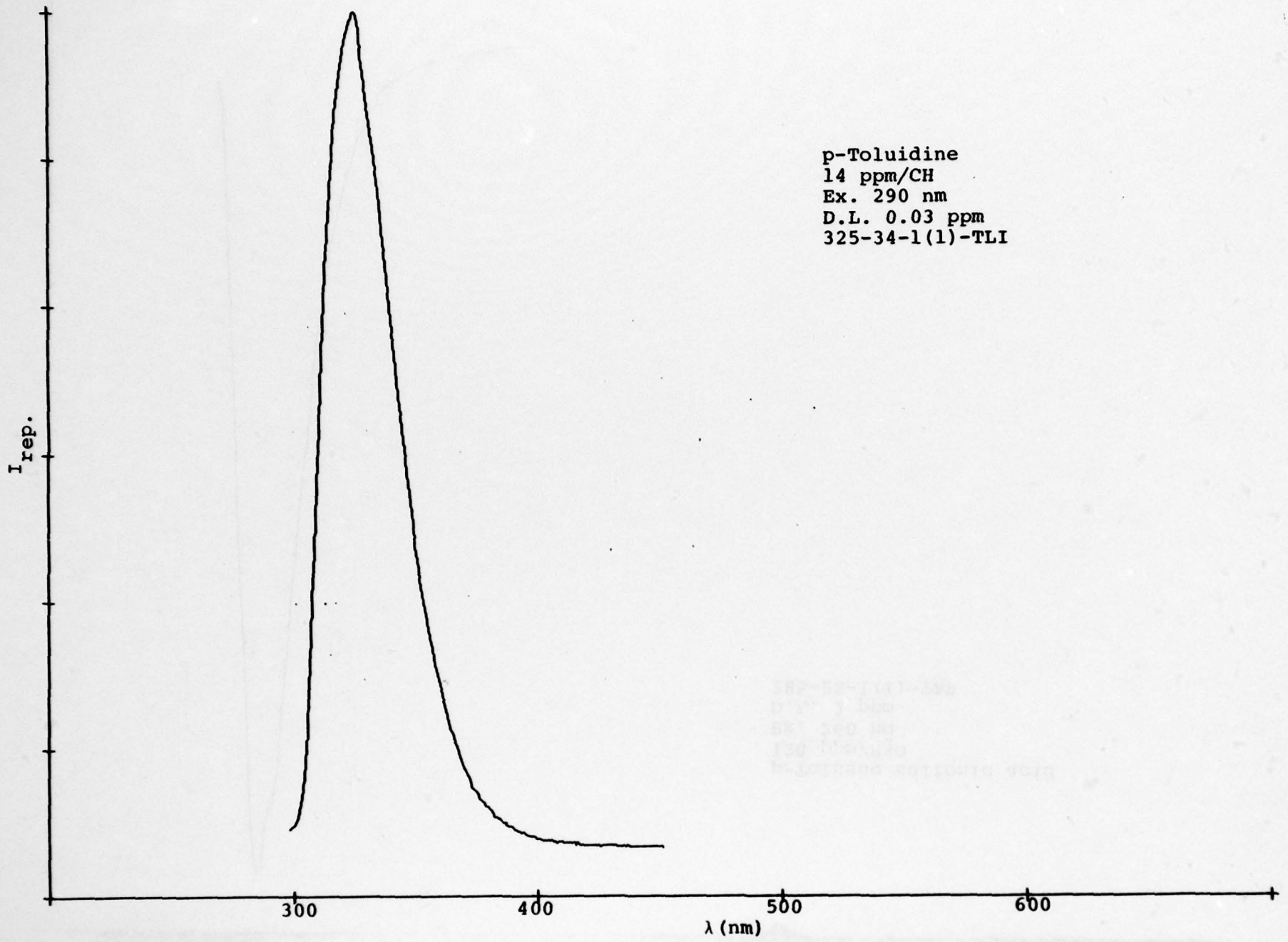
Water background for
Tannic Acid

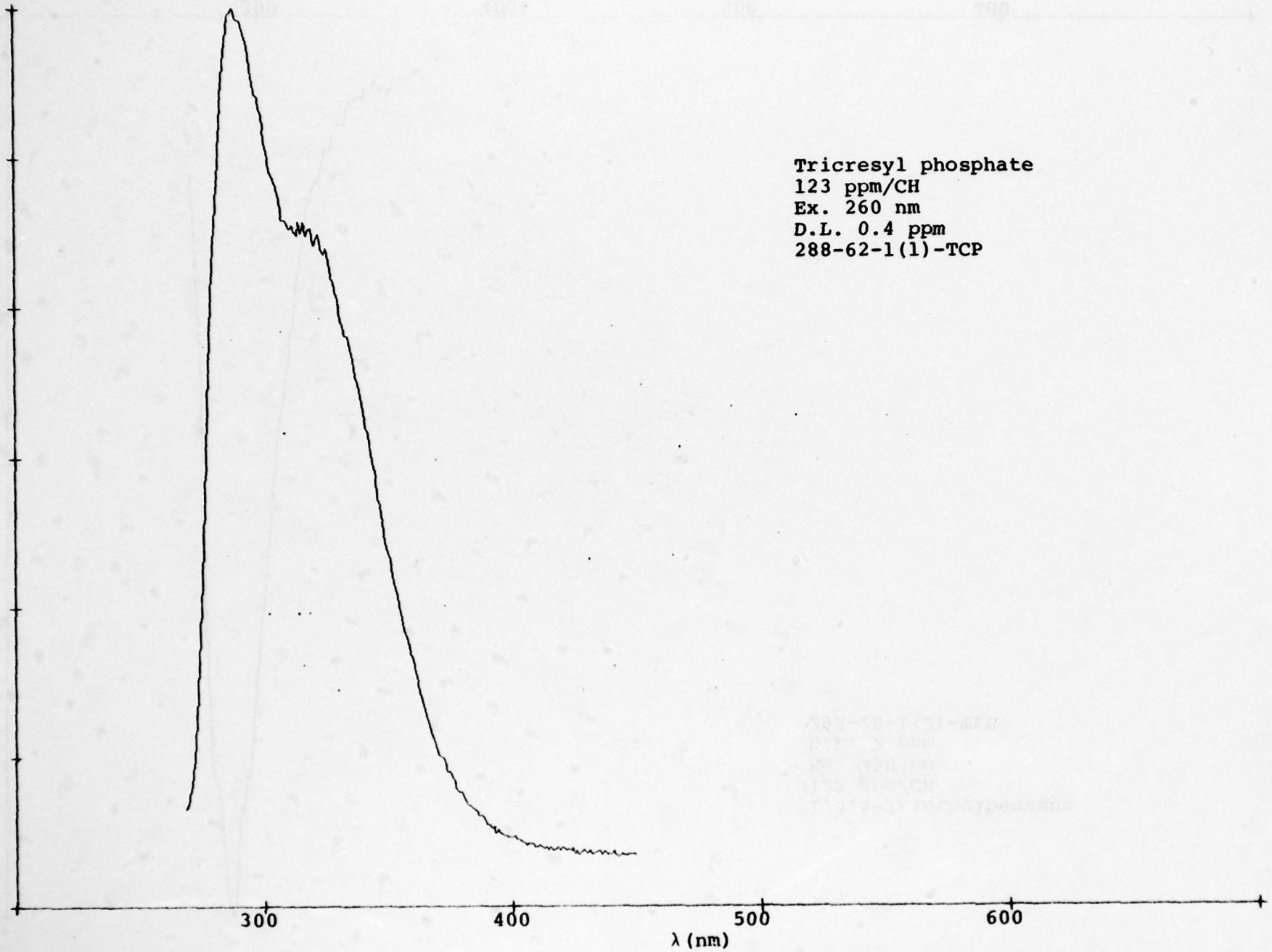


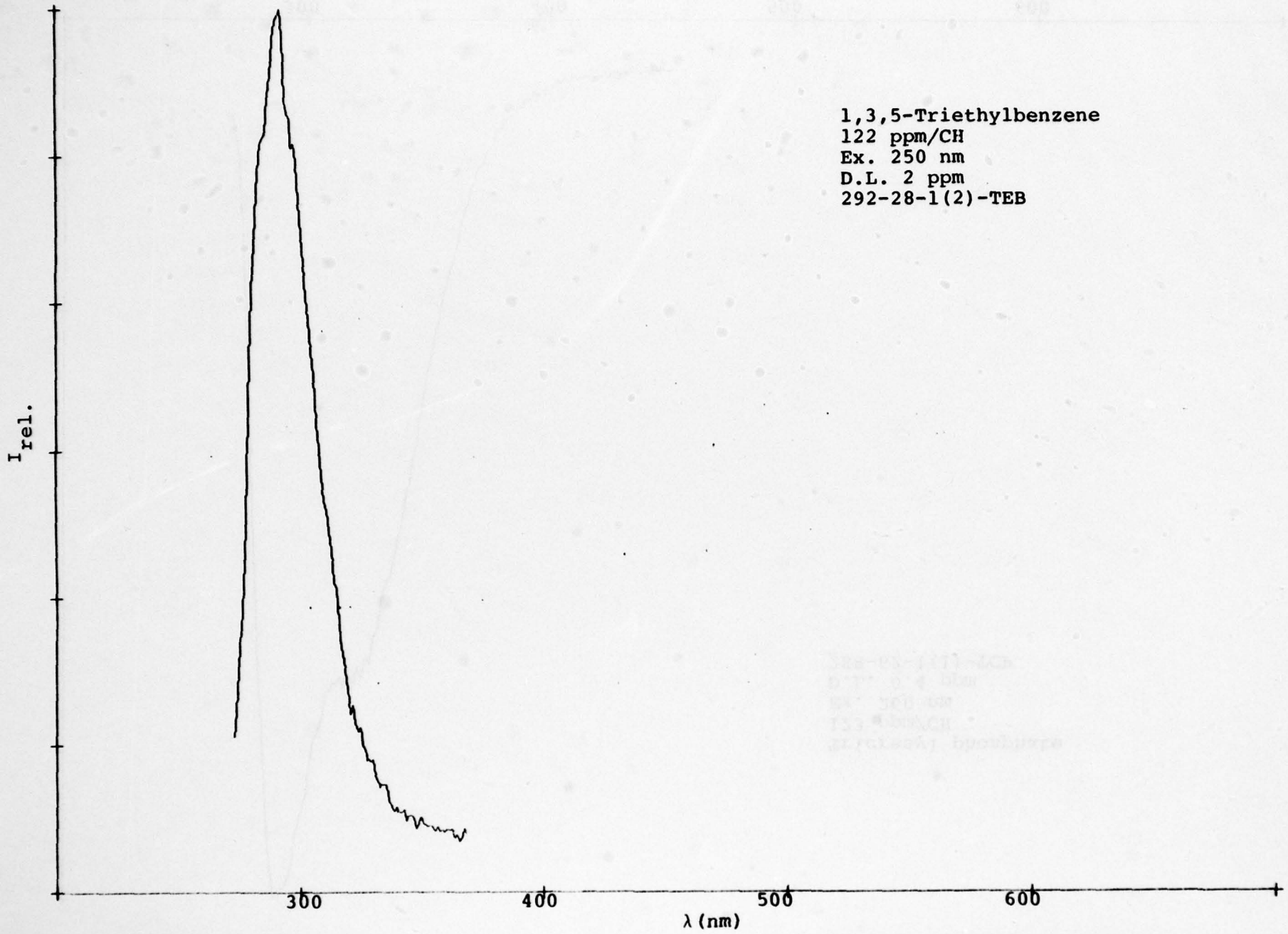

Tetrahydronaphthalene
12 ppm/CH
Ex. 260 nm
D.L. 0.1 ppm
284-27-1(2)-THN
I rel.
300
400
500
600
λ (nm)

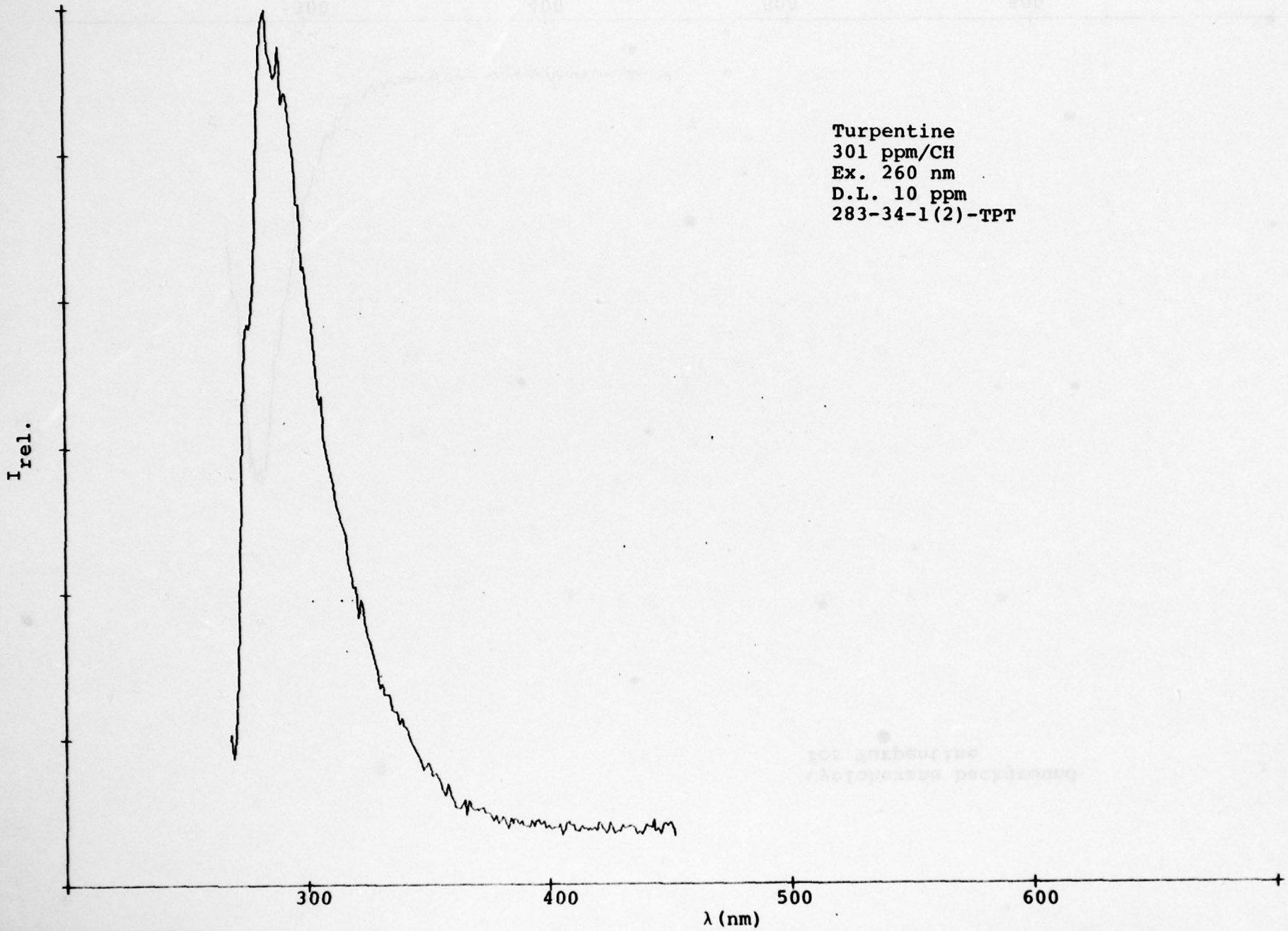

Toluene
110 ppm/CH
Ex. 250 nm
D.L. 2 ppm
284-27-2(2)-TOL
$I_{rel.}$
300
400
500
600
λ (nm)


p-Toluene sulfonic acid
120 ppm/H_2O
Ex. 260 nm
D.L. 2 ppm
285-28-1(1)-TAP
$I_{rel.}$
300
400
500
600
λ (nm)

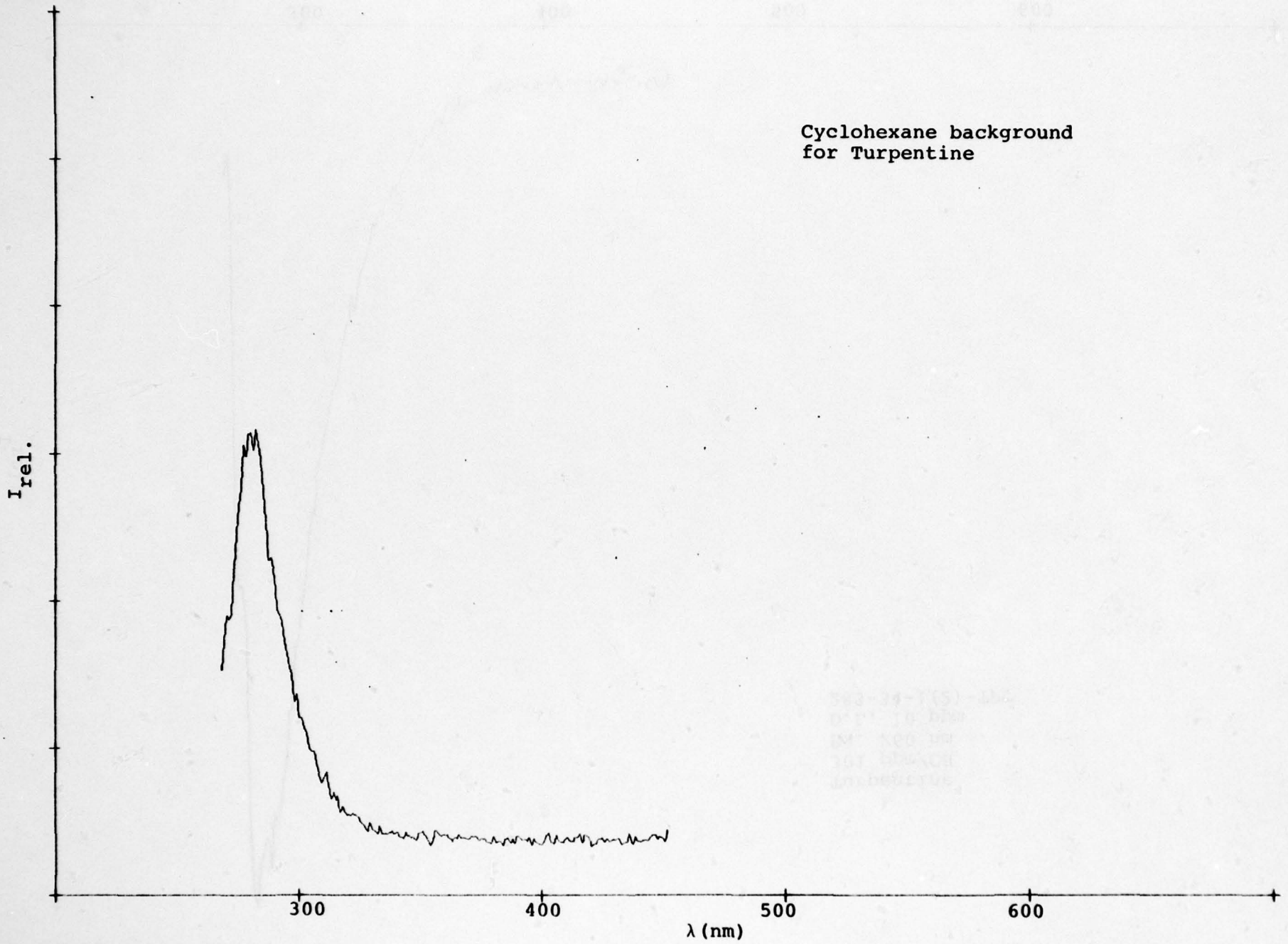

p-Toluidine
14 ppm/CH
Ex. 290 nm
D.L. 0.03 ppm
325-34-1(1)-TLI
$I_{rep.}$
300
400
500
600
λ (nm)

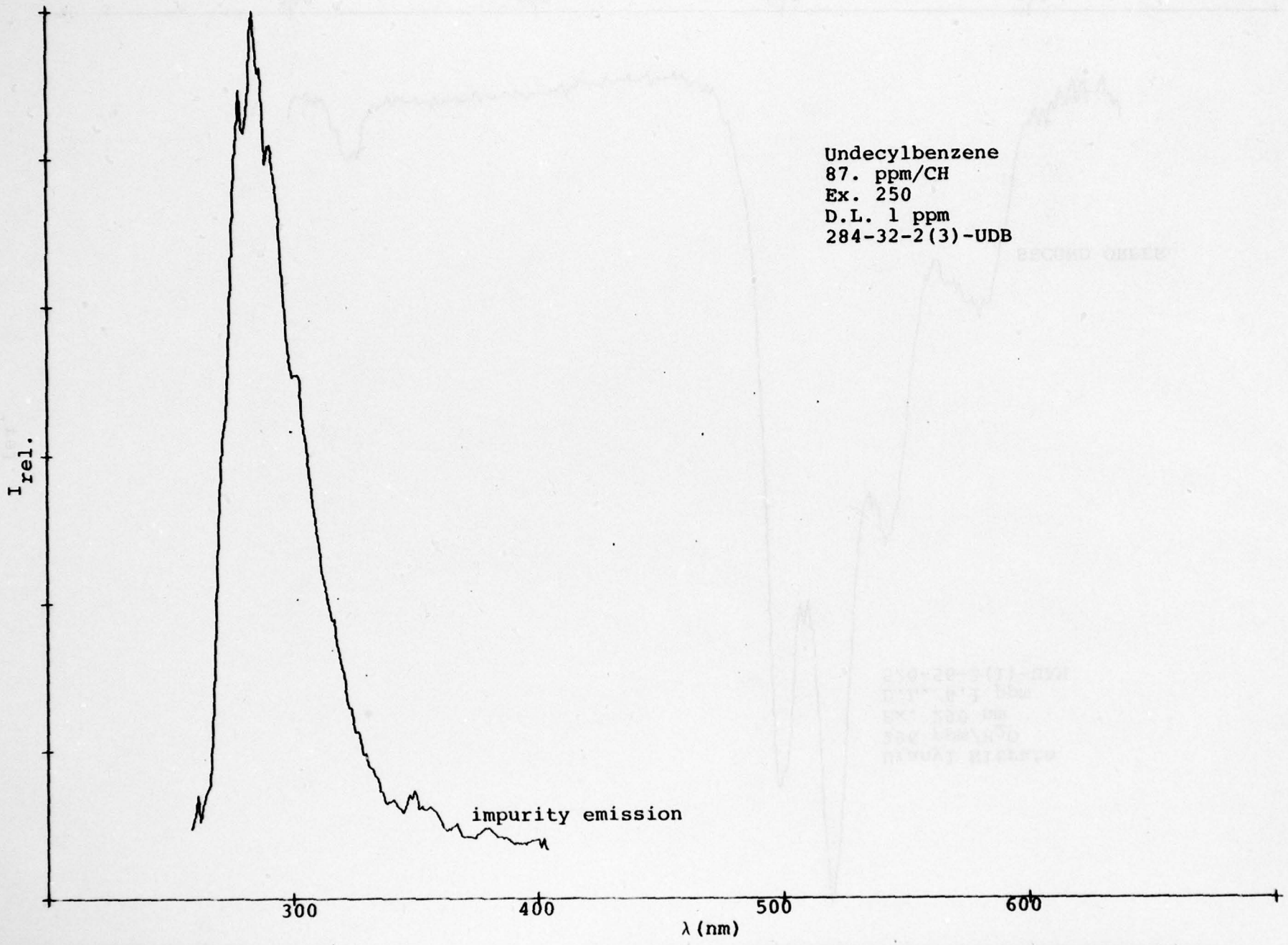

Tricresyl phosphate
123 ppm/CH
Ex. 260 nm
D.L. 0.4 ppm
288-62-1(1)-TCP
300
400
500
600
λ (nm)

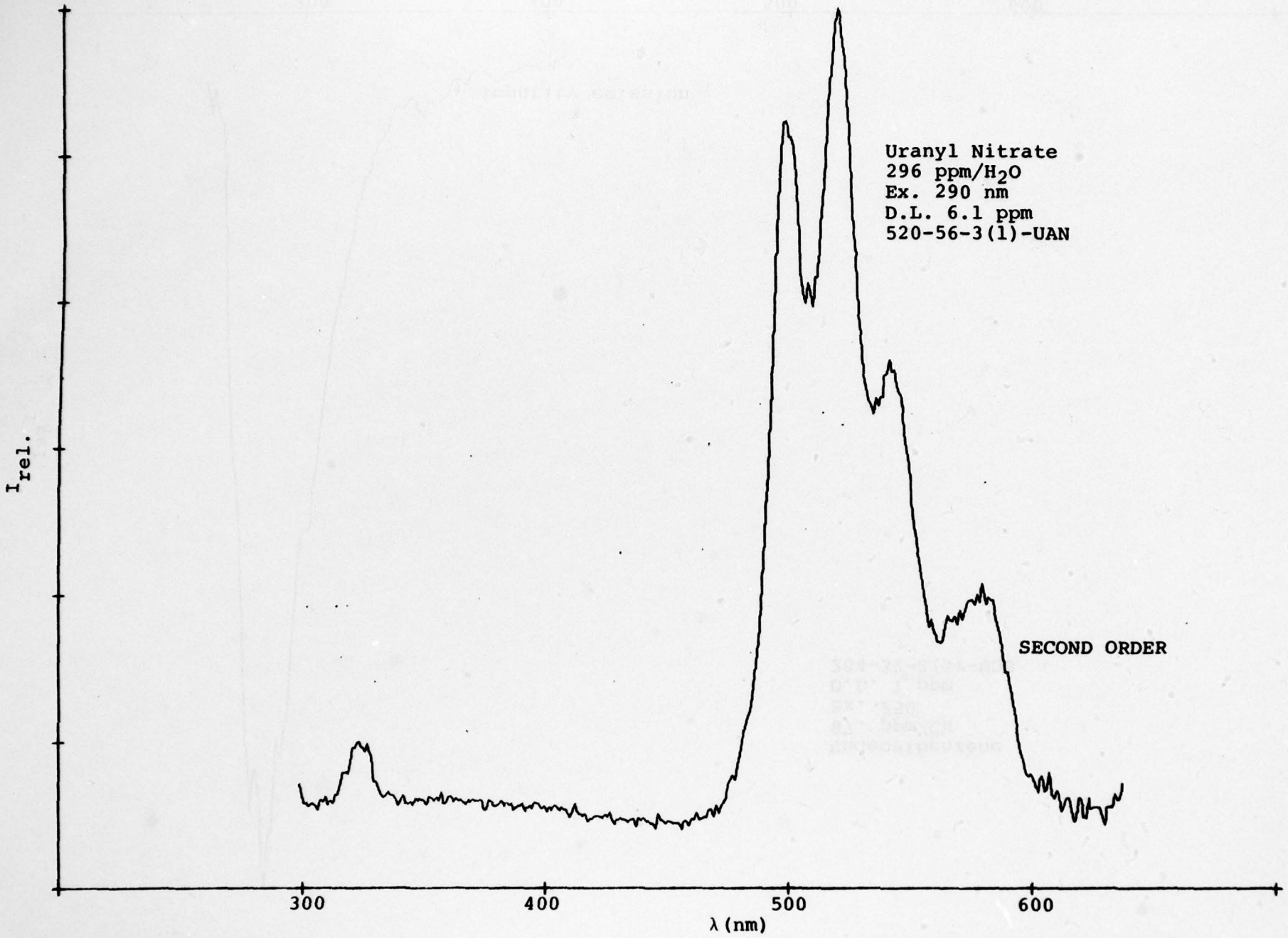

1,3,5-Triethylbenzene
122 ppm/CH
Ex. 250 nm
D.L. 2 ppm
292-28-1(2)-TEB
$I_{rel.}$
300
400
500
600
λ (nm)

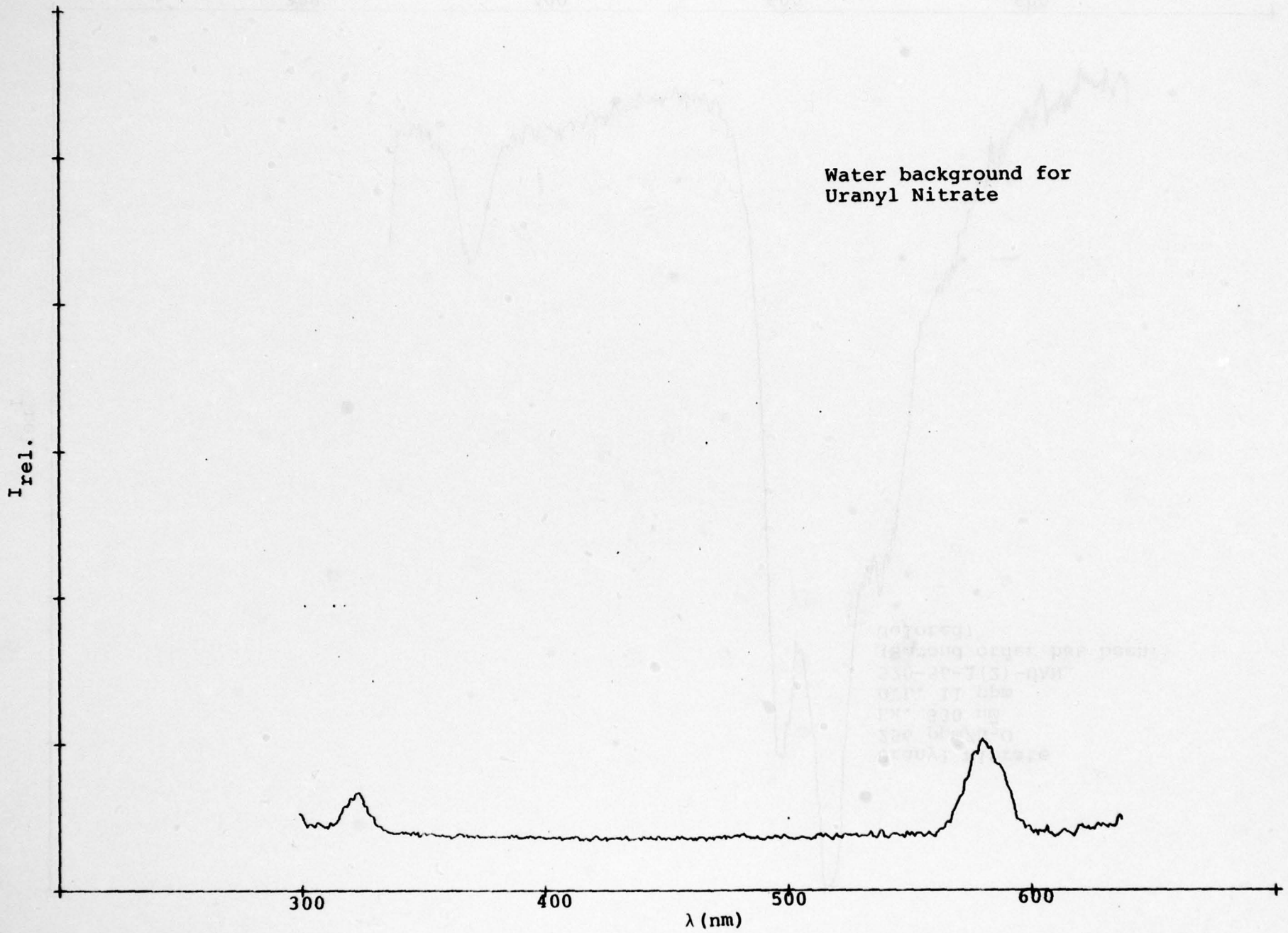

Turpentine
301 ppm/CH
Ex. 260 nm
D.L. 10 ppm
283-34-1(2)-TPT
$I_{rel.}$
300
400
500
600
λ (nm)

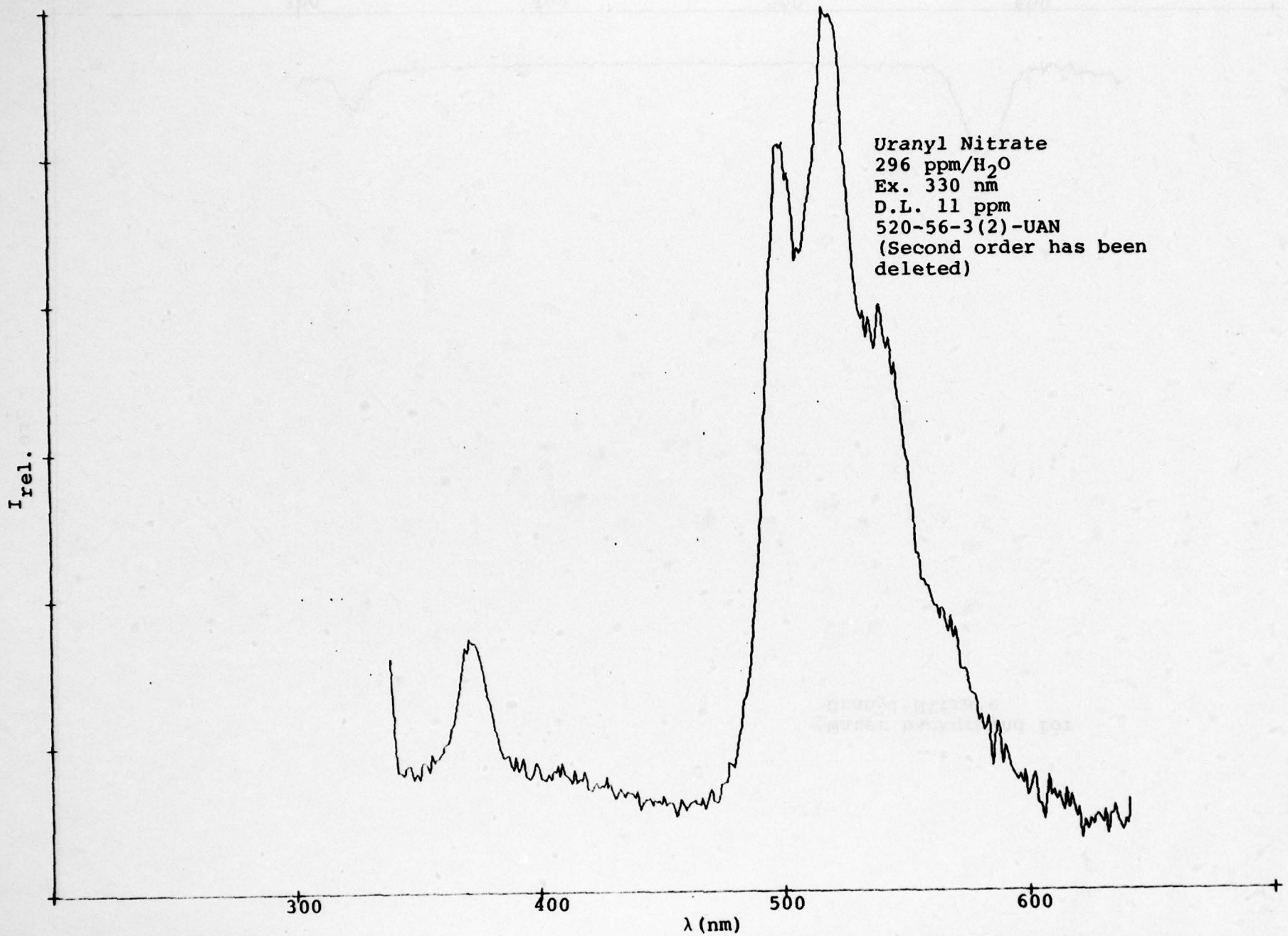
Cyclohexane background
for Turpentine

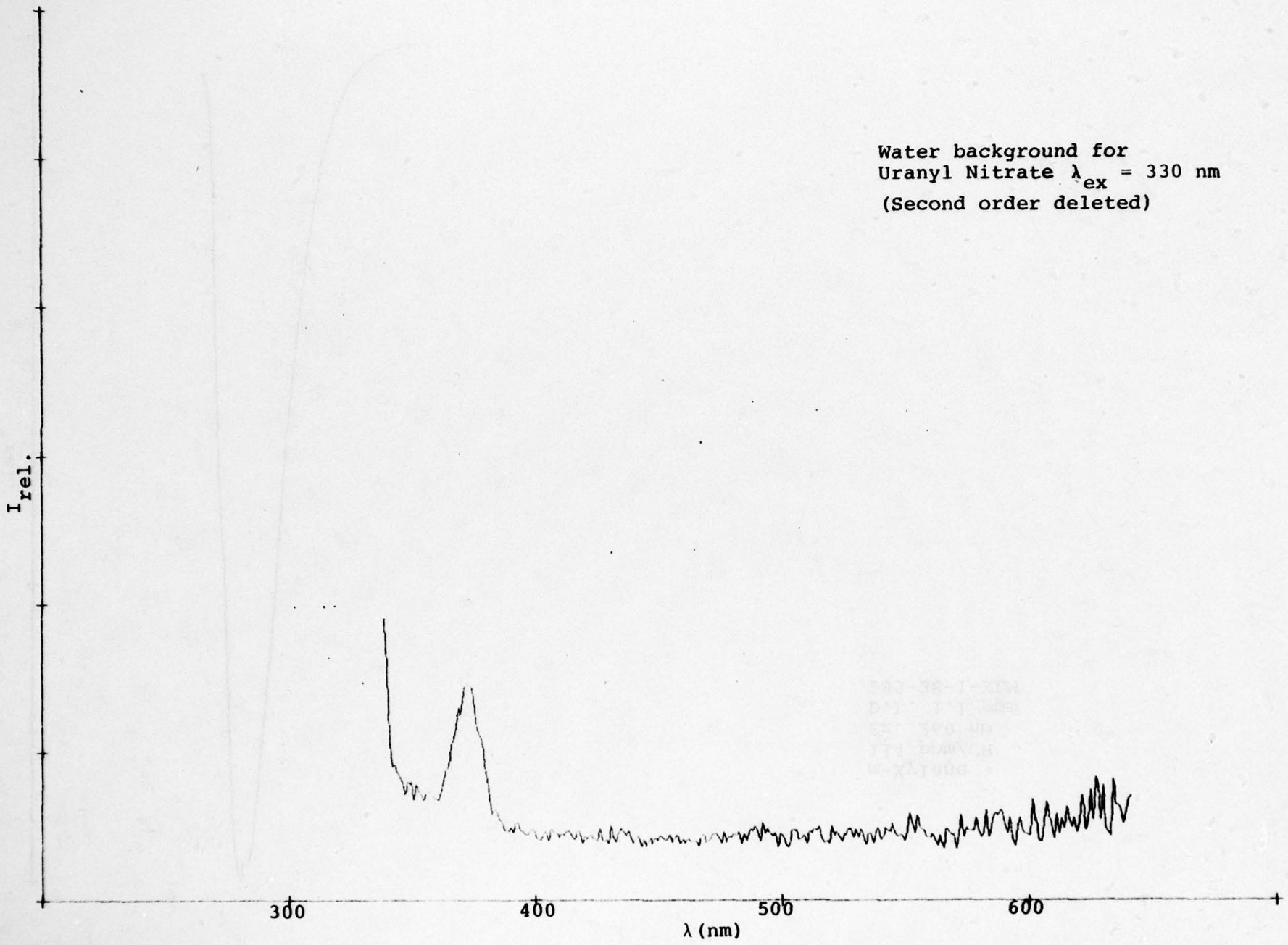


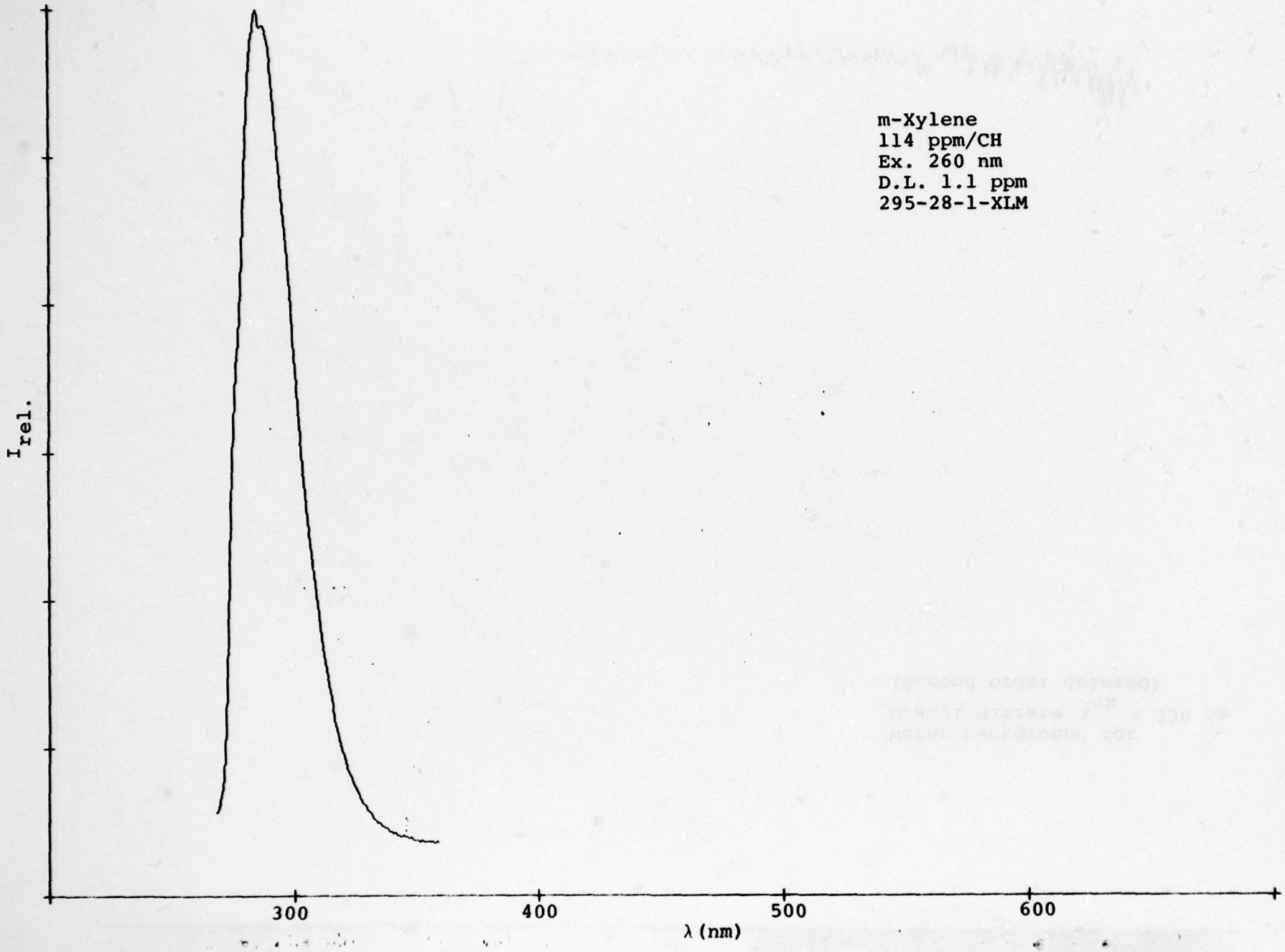

Undecylbenzene
87. ppm/CH
Ex. 250
D.L. 1 ppm
284-32-2(3)-UDB
I rel.
impurity emission
300
400
500
600
λ (nm)

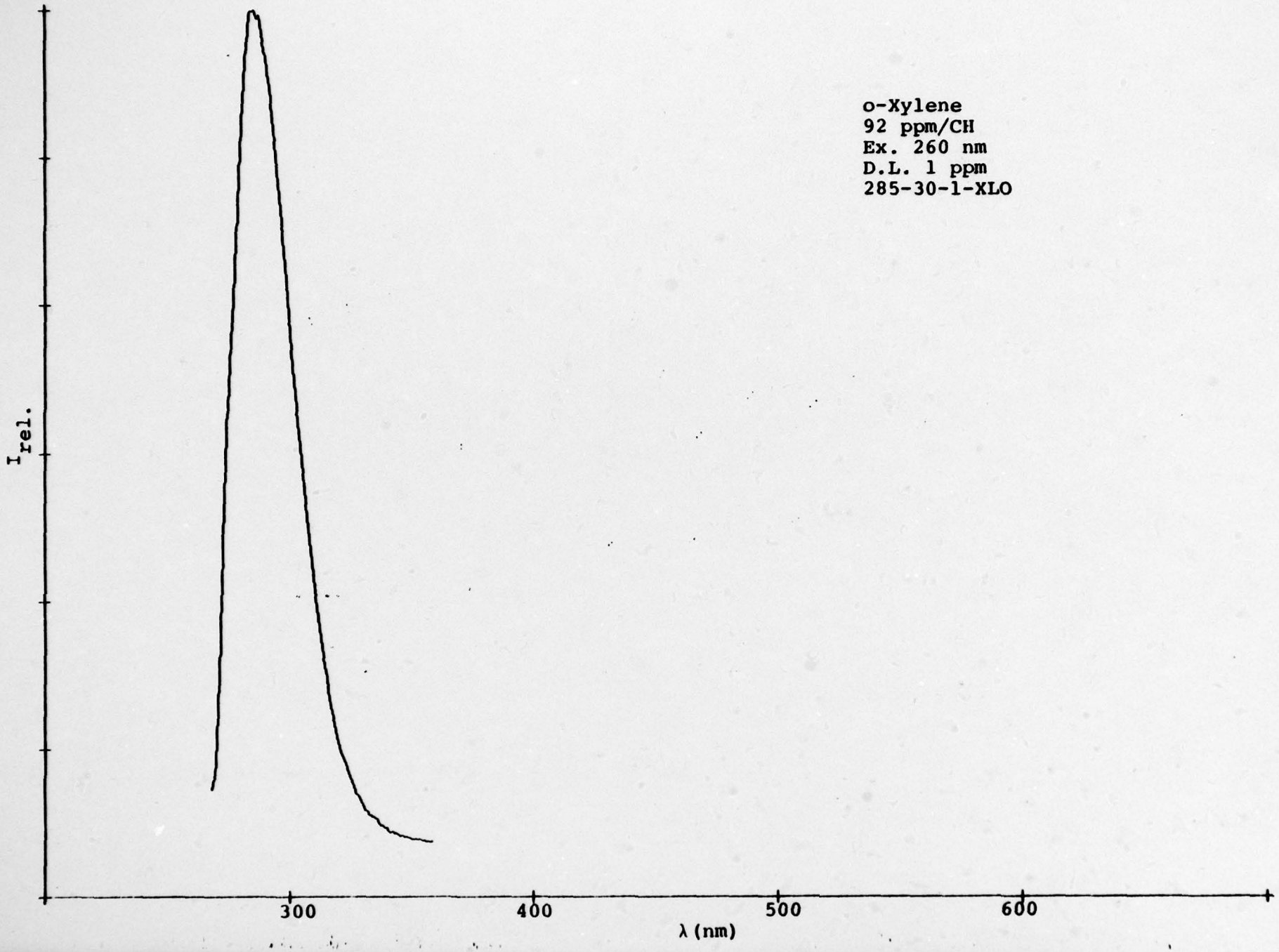

Uranyl Nitrate
296 ppm/H_2O
Ex. 290 nm
D.L. 6.1 ppm
520-56-3(1)-UAN
SECOND ORDER
$I_{rel.}$
300
400
500
600
λ (nm)


Water background for
Uranyl Nitrate
$I_{rel.}$
300
400
500
600
λ (nm)


Uranyl Nitrate
296 ppm/H_2O
Ex. 330 nm
D.L. 11 ppm
520-56-3(2)-UAN
(Second order has been deleted)
$I_{rel.}$
300
400
500
600
λ (nm)


Water background for
Uranyl Nitrate λ_{ex} = 330 nm
(Second order deleted)
$I_{rel.}$
300
400
500
600
λ (nm)


m-Xylene
114 ppm/CH
Ex. 260 nm
D.L. 1.1 ppm
295-28-1-XLM
$I_{rel.}$
300
400
500
600
λ (nm)


o-Xylene
92 ppm/CH
Ex. 260 nm
D.L. 1 ppm
285-30-1-XLO
$I_{rel.}$
300
400
500
600
λ (nm)